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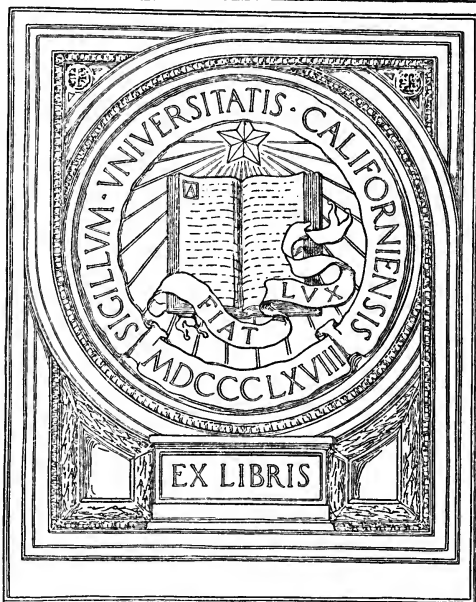


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AN INTRODUCTION
TO
CHEMICAL ANALYSIS

ROCKWOOD

AN INTRODUCTION
TO
CHEMICAL ANALYSIS

FOR STUDENTS OF MEDICINE, PHARMACY
AND DENTISTRY

BY

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MANUAL OF PHYSIOLOGICAL CHEMISTRY"

California College of Pharmacy

FOURTH REVISED EDITION
WITH 20 ILLUSTRATIONS

PHILADELPHIA
P. BLAKISTON'S SON & CO.
1012 WALNUT STREET

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PREFACE TO FOURTH EDITION

ADVANTAGE has been taken of the exhaustion of the last edition to make such alterations as appeared desirable without materially changing the original plan and scope of the book—that is, to leave it an introductory guide for the first-year college student. The changes are chiefly the simplification of methods where experience has shown that the student is most likely to have difficulty, together with the correction of a few errors. For suggestions I have been indebted to instructors in this department, particularly to Mr. J. E. Booge.

THE UNIVERSITY OF IOWA.

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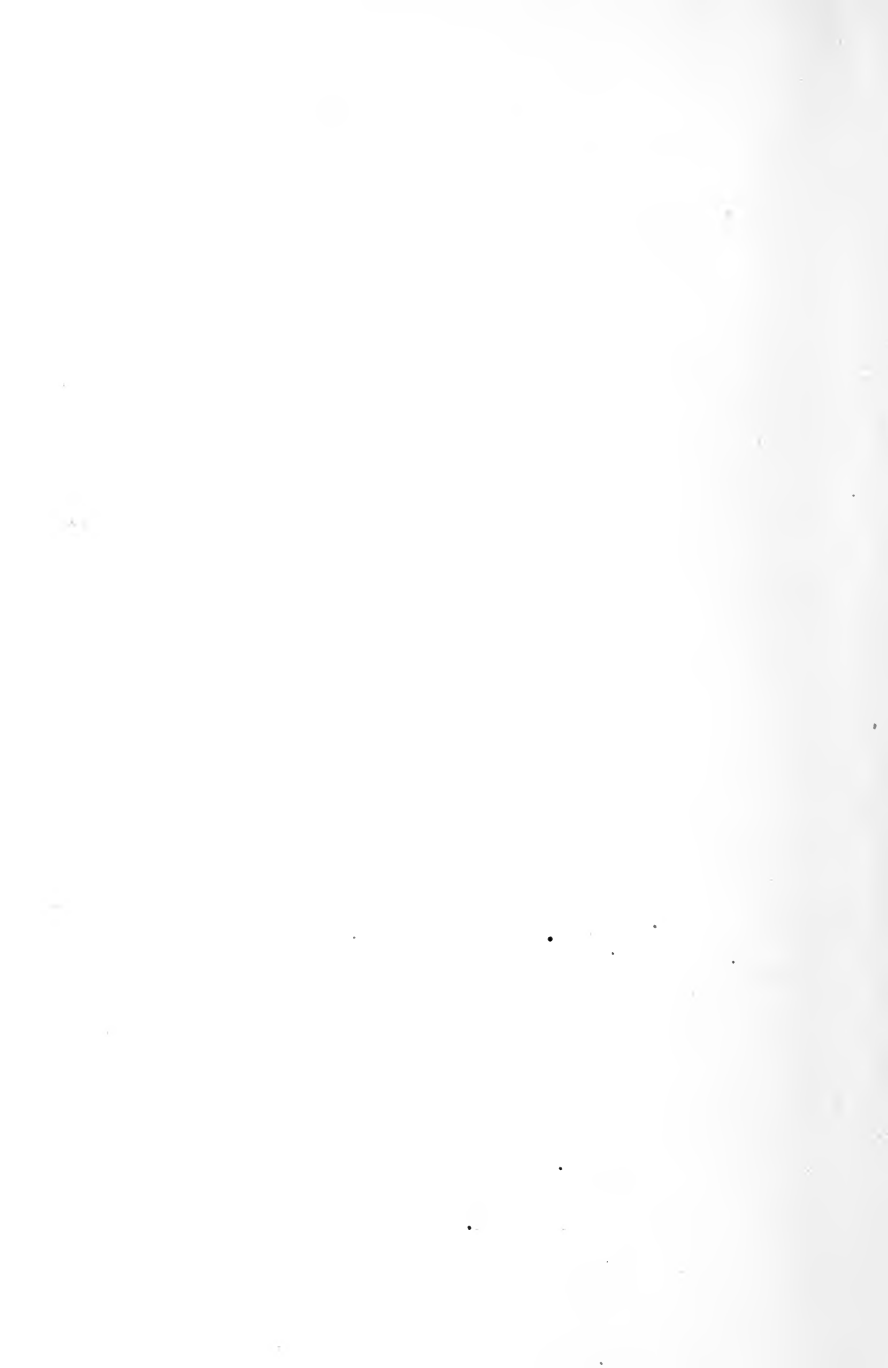
PREFACE TO THIRD EDITION

WITHIN the last few years the methods and theories of physical chemistry have been more and more successfully applied in different fields of medicine. Among the theories which have been most fruitful in results stands prominently the ionic theory of the nature of solutions and the action of many classes of dissolved compounds. It is self-evident that a knowledge of this is a necessity for those who wish to acquire an acquaintance with chemistry from the present-day standpoint or to keep pace with its developments. The surest means of gaining familiarity with these conceptions is by applying them practically in every-day work.

In the present revision of this book, therefore, greater prominence than before has been given to the ionic explanations of analytical reactions. This has been done partly because of the clearness with which such explanations can be made and partly to enable the student to assimilate the general theory. At the same time it has not been thought best to wholly abandon the older terminology which is still largely used in medical science.

The arrangement of the work has otherwise been changed but very little. No attempt has been made to produce a complete manual of qualitative analysis, but rather to provide such an introduction to the subject as may show its application to other branches of science and perhaps lead the student to a desire for a more extended course.

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PREFACE TO FIRST EDITION

ALTHOUGH it may be desirable that elementary chemistry should be completed before the professional college is entered, this is impractical in case of many American schools. The value of analytical chemistry in stimulating observation, power of discrimination, independence and self-reliance has long been recognized, as well as its services in affording an easy introduction to chemical work. It may, however, be carried on as a handicraft, without being of assistance in demonstrating the fundamentals of chemistry. The medical student not infrequently regards it as of no value except for the purpose of making analyses and for these he believes he will have little use. Though the importance of chemical analysis *per se* will probably always be slight, its points of contact with the other subjects in the medical curriculum are so numerous that, when rightly carried on, it not only stimulates interest in its own pursuit, but gives a mastery over other branches which can be as easily attained in no other way.

The chemical incompatibility of medicinal substances is so intimately related to their chemical reactions that for their intelligent use a thorough acquaintance with the latter is a prerequisite. The same is true of the chemical antidotes for poisons. For this reason the reactions are quite fully given here. The properties and methods of manufacture of many substances employed for medical or dental purposes are also illustrated by the analytical reactions, which can therefore be used to impress them upon the mind of the student and thus make a connected chain of what is often learned as dismembered facts.

It is natural that chemical analysis for beginners should be differently conducted with professional students than with those who do not desire to apply it to any particular branch of knowledge. This book has been arranged for students of medicine, pharmacy, and dentistry, much of whose territory is common. It assumes that some study has been devoted to general chemistry or that this is a contemporaneous course. It is designed to furnish a scientific basis for more technical courses but not to supplant these, and to give the familiarity with chemicals and manipulative methods, which is so necessary for real success in some lines of medical work.

There is no intention to make of the student an analytical chemist or mere mechanical manipulator. In many cases the work is abridged, as in the detection of poisons, where only the principal ones are considered or those which best illustrate the methods of such analysis. At the same time no attempt has been made so far to cut down the work that, with a mere smattering of knowledge, the student finishes, believing himself competent to meet all problems that he may encounter.

To accomplish the purpose outlined, series of questions have been inserted. The answers to these may be found partly in the experimental work previously done, and partly through reading in other departments of chemistry or of medicine. Others will suggest themselves to the instructor, and it is only by insisting upon such outside study that the greatest value can be gained from such a course as this. If followed out they are a stimulus to individual application, they prevent mechanical working without thinking, and, by connecting chemical analysis with general chemistry, materia medica, physiology, toxicology, and other departments of medicine, they help to make clear the unity of the complete course.

But few equations have been given, and those usually only the more difficult ones. These benefit the student only when he can write them for himself and he should do

this as far as possible in the time allowed. For a similar reason no tables are given for finding without labor the results of volumetric analyses. To represent the metric system as something more than a theory and to prepare for its future practical use all measurements are stated in metric denominations. Degrees of temperature are given by the centigrade thermometer.

While the length of the medical course often forbids any extended work in quantitative analysis, some practical work in this is indispensable, partly in order to familiarize the student with principles, partly because of its applications to other departments of medicine. Volumetric methods are admirably adapted for both these purposes and enough are given to illustrate the more common and to indicate how they may be extended. They include the preparation of the standard solutions, as well as the use of these, to that the student may, if necessary, be in condition to undertake the whole process in the practice of his profession and not be reduced to a state of helplessness if the emergency should arise. For the same reason, in a special table is included the preparation and testing of the qualitative reagents.

To make the course more interesting, by showing some of its applications, chapters are added on the testing of water, the detection of poisons, and analysis by means of the blow-pipe. While the latter is of subordinate importance for students of medicine and pharmacy, it has, in this laboratory, proved itself of value in demonstrating to students of dentistry the physical and chemical properties of the metals and their alloys in a manner not possible by wet methods of testing. The length of the course can be modified to fit the curriculum by omitting the less important parts or by varying the number of unknown substances to be analyzed under the separate divisions of the subject.



TO THE STUDENT

1. PERFORM no operation without a reason. Ask yourself in advance the object, and afterward what has occurred; for example, in precipitating or washing—what is removed? what remains?

2. Do your own work; use your own judgment, and let your neighbor do the same.

3. Avoid the use of an excess of materials or reagents. Add the reagent slowly, as much as is necessary and no more. Do not use concentrated acids unless they are specifically called for.

4. When a strongly acid solution, or one which gives an offensive odor is to be boiled, or when any acid solution is to be evaporated, do this under a hood that the gases may not remain in the room.

5. Except for cleaning, always use distilled water.

6. Always use pure chemicals for reagents, but never be sure that they are so without proving them.

7. Never put platinum wire, stirring rod or other object into a reagent bottle. Do not return to the bottle any reagent that has been removed.

8. In using the reagents never lay the stopper down. Hold it between the second and third fingers and replace it immediately in the bottle.

9. Do not throw into the sink concentrated acids, strong solutions of mercury, or solid refuse like broken glass or filter-paper. Put them in the waste jar.

10. Too great care cannot be exercised as to cleanliness. Have a cloth or towel and keep apparatus and desk in good order. Each student will be held responsible for the condition in which his desk is left.



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CHEMICAL ANALYSIS

INTRODUCTION

THE object of chemical analysis is the determination of the chemical composition of matter. This determination may be either of the kind of its components or of their amounts. The methods used for the former belong to qualitative analysis; for the latter to quantitative.

In qualitative analysis the substance studied is not only examined alone, but it is subjected to the action of certain forces or of chemical compounds called reagents. These are designed to make more evident the physical properties of the substance or to produce characteristic compounds or changes. All such phenomena, called the reactions of the substance, can be used in its identification. Before entering upon the practical work of qualitative chemical analysis some explanation is demanded relating to the apparatus and reagents most in use, to the common processes, and to some of the terms employed.

Solutions

In the majority of cases, although not always, the qualitative tests are made upon substances in solution. A solution is formed when a solid, liquid, or gas is taken up by a liquid so that it loses its usual physical properties and can no longer be perceived. Solutions are regarded as of two kinds, physical and chemical.

Physical solutions are similar to those which result from mixing salt or sugar with water. There is no apparent

chemical change in the substance dissolved, which is left unaltered when the solvent evaporates. In physical solutions of solids in liquids a rise in temperature, as a rule, increases not only the rapidity of solution, but also the amount of the solid capable of being dissolved. With solutions of gases in liquids the opposite is true and most dissolved gases will be driven out of solution by an increased temperature.

Chemical solutions are such as the one formed when metals are acted upon by an acid. The metals disappear but unite with the solvent so that when the latter evaporates an entirely different substance from the original one remains. In this case heating lessens the time of solution, but does not necessarily increase the amount of metal dissolved. In chemical solutions of gases, however, the gas is often expelled by heating, the compound being thus decomposed.

A concentrated solution is one in which the solvent contains a large amount of the dissolved substance (the solute); a dilute solution, one in which the amount dissolved is small. When the solvent contains as much of the solute as it can take up it is said to be saturated. A solution which has been saturated with a solid at a high temperature ordinarily deposits a part of the solid if the temperature falls. A few, as the temperature is decreased, will hold what has gone into solution, until the liquid is shaken or some solid matter is introduced, whereupon a large quantity of the dissolved material separates from the liquid. Solutions containing this excessive amount are said to be super-saturated. Where a solid remains floating in a liquid without dissolving it is said to be suspended or in suspension.

Most solids which have been dissolved in a liquid and which afterward separate through a change in temperature or a decrease in the volume of the solvent are crystalline in form. Such a method of preparation is called crystallization. A crystal is a solid which has a regular form bounded by plane

surfaces, the angles between these being constant for the same species of crystal. Large crystals are produced only when they form slowly. It has been found that impure solids after having been dissolved in water or other fluid and then allowed to crystallize leave most of their impurities in the liquid or "mother-liquor" so that this affords one of the best methods for purifying such substances.

The Heating of Liquids

For making solutions and for heating liquids the chemist commonly uses test-tubes, beakers or flasks of glass, or dishes of porcelain. Test-tubes are made of thin glass and are



FIG. 1.—*Apparatus for solution.* 1. Test-tubes in wooden support. 2. Beakers. 3. Iron stand with adjustable rings for supporting objects while they are heated. On one of the rings is a sand-bath. 4. Flasks.

designed to be heated in contact with the flame without breaking. The flame should, however, not be allowed to touch the tube above the liquid, since it easily becomes superheated there and breaks when moistened later. The heat should

not be applied to the bottom of the tube alone, as the steam bubbles thus produced might suddenly force the hot liquid from the tube, but all the parts of the liquid should be heated by moving and turning the tube in the flame. On account of this same danger the examinations of the boiling substance should be made from the side and never from above, and a test-tube while boiling should never be pointed toward another person. A tube half-full can be brought to the boiling point while it is held in the fingers, although holders are sometimes used. If one is desired it can be made from a strip of paper, which permits the rotation of the tube.

If long boiling is requisite a beaker is to be preferred to a test-tube. As these are somewhat thicker on the sides than at the bottom, they are not so well adapted to being heated in contact with the flame. They may be supported by an iron-wire gauze or plate, which can be heated to a low redness without danger to the beaker if it contains a liquid. As with any other glass vessels they should not be heated above the liquid. Instead of the gauze or plate, a sheet of asbestos is sometimes used or a sand-bath—that is, a shallow iron dish with a thin layer of sand which distributes the heat evenly to the vessel. The two latter, although they are safe, waste more of the heat than does the gauze. Glass flasks can be used in the same way as the beakers. Evaporation is less from these than from beakers, which is often desirable. All glass vessels composed of the ordinary German glass are somewhat attacked by boiling water, and especially so by alkaline solutions. If great accuracy is desired those made of a resistant glass should be substituted for the former. Dishes of porcelain are but little affected by the ordinary reagents even at the boiling-point, and the danger of their breaking is much less. A further advantage is that they may be heated with the naked flame. Liquids heated in them for a long time, however, suffer a considerable loss by evaporation.

Evaporation

Evaporation is the process by which a volatile substance is separated from a less volatile solid or liquid, the more volatile compound being allowed to escape. It may take place slowly at the ordinary temperature, as, for example, when tinctures become more concentrated, through loss of alcohol, by standing in open bottles. It is hastened by the higher

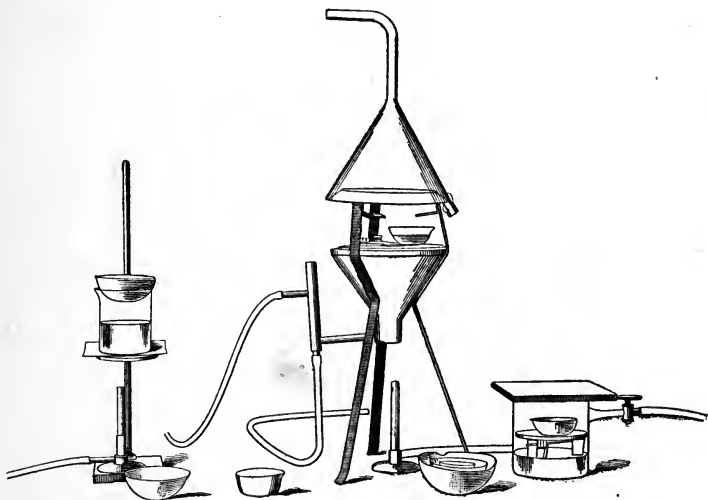


FIG. 2.—*Apparatus for evaporation.* 1. An extemporized steam-bath—a beaker of water on which a dish can be heated. 2. A copper steam-bath with tube supplying water and allowing the excess to escape, thus maintaining a constant level. The funnel above excludes dust. 3. A sulphuric acid vacuum-desiccator connected with air pump. In front are evaporating dishes of porcelain, platinum and glass.

temperatures and is most frequently carried on by this means in chemical operations. Thus it is made use of in removing from solutions an excessive amount of a volatile acid like hydrochloric, or even of one which is less readily converted to a gas, like sulphuric, in which case to effect its removal the liquid

must be evaporated to dryness. When a liquid is to be evaporated a wide and shallow dish should be used as the vapors most easily pass off from this. From a test-tube, on the other hand, evaporation is slow, the vapors condensing above to the liquid form, and flowing back into the tube. It is often advisable to conduct the process at some definite temperature, for instance not above 100° ¹ in order to avoid burning or de-

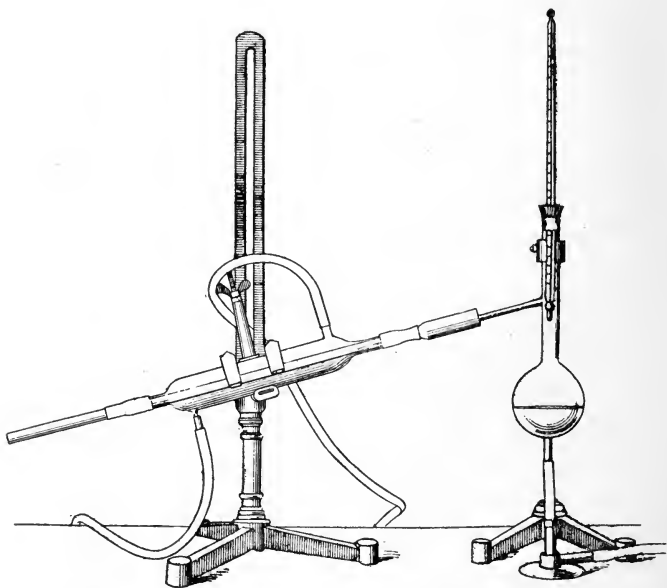


FIG. 3.—*Apparatus for distillation.* A flask connected with a Liebig's condenser and provided with a thermometer for showing the boiling-point of the liquid which it contains.

composition. This may be done by placing the liquid to be evaporated in a dish and setting this on a vessel in which water is boiling, known as a water-bath or steam-bath. For small operations a beaker will answer for the lower vessel.

¹ In this work all temperatures are given in the centigrade scale, where the freezing-point of water is at 0° and the boiling-point 100° .

All evaporations of injurious or offensive gases should be conducted in a hood or fume chamber—an enclosure connected with a ventilating shaft. Aqueous solutions can be evaporated at low temperatures by placing the dish over a vessel of some substance which has an affinity for moisture, like concentrated sulphuric acid, and placing over the whole an air-tight cover. This is called a desiccator. The process is much hastened by exhausting the air from the apparatus.

Distillation

Distillation is similar to evaporation except that the expelled volatile substance does not escape but is collected by being again condensed to a liquid through cooling. This is commonly effected by passing the vapors into a tube which is surrounded by circulating cold water. If a thermometer is suspended with its bulb in the vapor during distillation it indicates the boiling-point of the liquid. This, with the melting-point, is of the greatest value in the identification of many compounds, especially the organic ones. The melting-point is determined after heating a short, small glass tube to redness in the middle, then drawing it out to a very small diameter. A piece of this closed at the lower end holds some of the powder beside a thermometer-bulb in a liquid, like water or sulphuric acid. By heating gradually until the powder melts, then reading the temperature, its melting-point is ascertained.

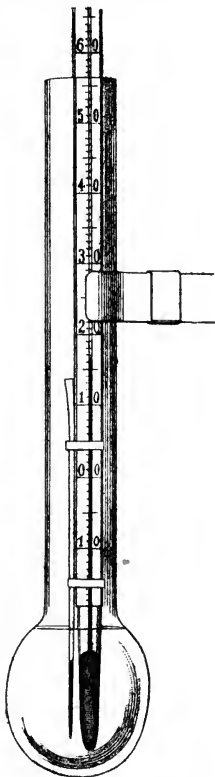


FIG. 4.—Apparatus for the determination of the melting-point of a solid.

Precipitation

Precipitation is the process of changing dissolved substances into the insoluble state. It may be without chemical change, as when the dissolved matters of tinctures are precipitated by water, simply because they are insoluble in the latter. Or, on the other hand, the precipitate may be a new chemical compound which has been produced by the mutual decomposition of two dissolved substances, as when red mercuric iodid is formed by mixing a solution of potassium iodid with one of corrosive sublimate. Both varieties of precipitates are important in medicine and pharmacy, but the latter will be the ones most frequently illustrated in qualitative analysis. They are usually heavier than the surrounding liquid and consequently settle to the bottom, but some of the flocculent kinds float for a long time before sinking. Precipitation is valuable as a means of identifying an unknown metal, since by this means characteristic compounds often appear; it is used to separate one substance from another by converting the one into an insoluble form; it is also of use in the preparation and purification of medicinal as well as other substances. Thus by the addition of a soluble carbonate to a calcium solution "precipitated chalk," a very pure form of calcium carbonate, is produced. When used in separation the filtrate must always be tested with more of the reagent in order to be certain that precipitation is complete.

Filtration

A precipitate or other undissolved solid can be separated from a liquid in which it is suspended by filtration. To accomplish this the mixture is poured upon some porous material which allows the fluid to pass through but retains the solids. A porous paper is the most common filtering agent. It is supported in a glass funnel of such an angle that if a cir-

cular piece of the paper is folded in the center and then again in the center at right angles to the first fold it will when opened make a cone-shaped paper funnel which fits the glass exactly. To obtain the most rapid and clean filtration it should be made to adhere to the sides of the funnel by moistening it with fluid of the same kind as that to be filtered and pressing it against the glass. It ought to be of such a size as not to reach quite to the rim of the funnel. The only ones of the common reagents which attack the cellulose of which the paper is composed are concentrated acids or strong solutions of sodium hydroxid or potassium hydroxid. The cheaper filter-papers contain compounds of the metals, such as calcium and iron, and these may be dissolved by reagents which are being filtered, thereby rendering the latter impure. Where great accuracy is important the paper is, therefore, previous to being used, washed with hydrochloric or hydrofluoric acid to remove impurities.

When it is desired to obtain the solution—called the filtrate—as quickly as possible without saving the precipitate, the plaited filter can be employed. This is made by folding double as before, and then into eight or sixteen folds, bending the paper each time in the same direction. Then each division is folded in the opposite way, without pressing at the tip, to avoid breaking, so that the filter looks like a closed fan. When it is opened the hollow cone has fluted sides, giving twice the surface of the plain filter. A plug of absorbent cotton loosely placed in the funnel is also convenient for obtaining the filtrate when the precipitate is to be discarded. Cotton consists, like the paper, of cellulose. Liquids which decompose cellulose should be filtered through asbestos or glass wool.

Many precipitates are so gelatinous that they clog the filter and the filtration proceeds very slowly. By passing the stem of a funnel through a rubber stopper into a vessel in

which a partial vacuum can be created, the solution can be more rapidly drawn through the filter. The air may be exhausted from the vessel below by means of a filter pump or aspirator attached to the water faucet of the laboratory. To avoid breaking the paper its tip must then be supported by inserting below it in the funnel a cone of platinum, muslin or some other strong material or a specially toughened paper must be employed. It should be remembered that a hot solution generally filters more rapidly than a cold one.

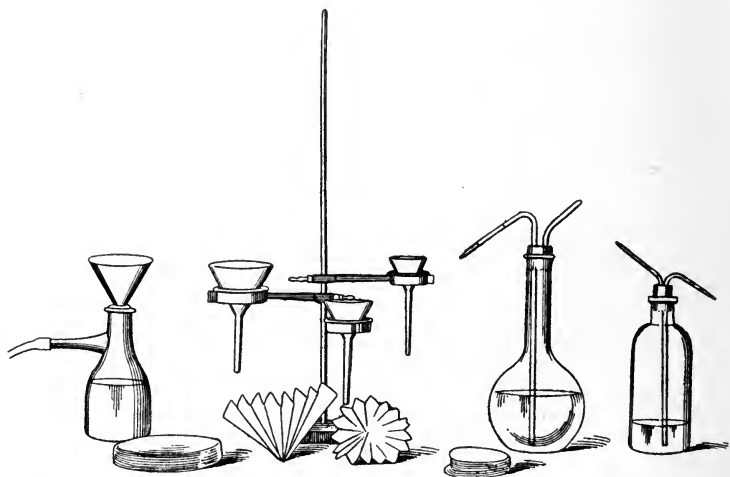


FIG. 5.—*Apparatus for filtration.* 1. A funnel fitted to filtering a flask which is connected with a pump for the production of a vacuum and consequently an increase in the rapidity of the filtration. 2. A support holding funnels for filtration. 3. Washing bottles. In front are packages of filter-paper with two plaited filters.

After the precipitate has been collected on the filter it is usually necessary to further purify it by removing the liquid with which it is saturated and which contains soluble matter. This is done by washing, generally using for this purpose distilled water, the hot being ordinarily preferable to the cold. The water may be poured on from any vessel, but is most

conveniently applied from a washing-bottle. This is constructed of a bottle with a stopper perforated with two holes. Through one a long, bent tube passes to the bottom. It is contracted to a narrow opening at the outer end and serves for the exit of a jet which is forced out by blowing into the other opening through a short tube. By such a small stream the precipitate can be thoroughly mixed with the water and if so desired, can be rinsed from the paper. For cold water any thick glass bottle of convenient size will serve, but if it is to be heated a thin bottomed flask must be employed. Washing with hot water is more effectual than with cold. To ascertain whether the washing is complete a drop of the filtrate can be evaporated on a platinum foil and the amount of dissolved matter observed.

Sometimes when, in spite of the above methods, the filtration is very slow, it may be better to wash by decantation—that is, by letting the precipitate settle, pouring off the liquid without disturbing the solid and repeating as many times as is necessary. With heavy compounds like those of mercury this can be done very rapidly.

Chemical Changes at High Temperatures

In order to produce certain chemical changes, or in the preparation of some substances, a higher degree of heat is required than that of boiling water. Even fusion or melting may be necessary. In many qualitative tests where small quantities of material are used the substance may be supported on a piece of charcoal, porcelain or platinum. The first necessitates the aid of the blowpipe; the second breaks too easily; the third is preferable because, while it is itself affected by few reagents and there is no danger of breaking, it permits a high heat to be attained. A pair of forceps or tongs will support it long enough in the flame to accomplish

the fusion. With large quantities of material, or where the heating must be long-continued a crucible can be advantageously substituted. These are most commonly made of platinum, porcelain, or clay.

Platinum is attacked by chlorin or by any mixtures, like aqua regia, which produce it. This is true not only during fusion, but from solutions at low temperatures. It will also be affected by heating with fusible metals, since these form alloys with it. Reducible compounds of such metals mixed

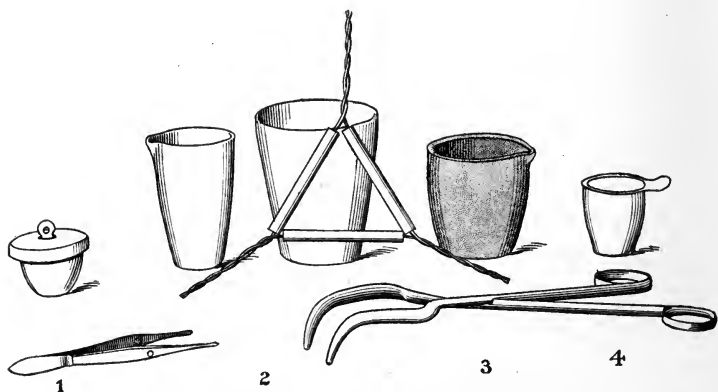


FIG. 6.—*Apparatus for fusion.* 1. Porcelain crucible. 2. Hessian or clay crucibles with a pipe-stem triangle leaning against the middle one. On this the crucible can be supported while it is heated. 3. A graphite crucible. 4. A platinum crucible with cover. In front are forceps and crucible tongs.

with carbon should not be heated in platinum nor should the fusible sulphids or the caustic alkalis, all of which combine with it.

In the absence of illuminating gas, the alcohol lamp will serve as a source of heat since it does not smoke cold objects held in the flame, while giving a great deal of heat. With gas, which is more convenient as well as cheaper than alcohol, the Bunsen burner is used. This consists essentially of a base, from which the gas is delivered by a small opening, and

above this a tube with openings near the base through which is admitted the air which then mixes with the gas. This mixing brings about the complete combustion of the carbon compounds of the gas, none being left to be deposited as soot, a high temperature being thereby produced. The openings below should be so regulated as to allow entrance to enough air to change the color of the flame from a yellow to a light blue. More than this lowers the temperature. With an ex-

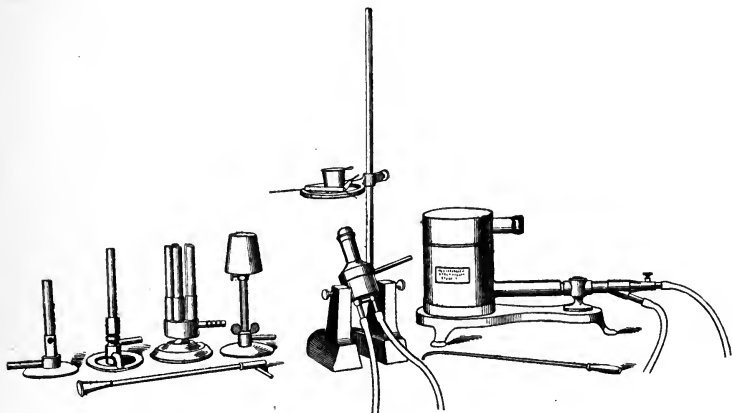


FIG. 7.—*Sources of heat.* 1. Two forms of Bunsen burners. 2. A cluster of five Bunsen burners for greater heat. 3. A Bunsen burner with iron chimney to shut off drafts of air. 4. A blast lamp in position to heat the platinum crucible above. 5. A gas furnace for more intense heat with larger crucibles. In front are two forms of blowpipes.

cess of air, too, the flame often “strikes back” or burns within the tube at the bottom, changing in color first to a yellow, afterward to green. In this case the gas must be turned off, the size of the air vents reduced and the burner relighted.

For higher degrees of heat the blast-lamp will be advantageous. This is similar to the Bunsen burner, except that the air is forced in through one tube while the gas enters by another, the two mixing just before they are burned. A bellows or water-blast will furnish enough air for this. For

large crucibles there is less waste of heat if the crucible is surrounded by a fire-clay box or furnace and the flame from the blast-lamp is forced in below.

For the better examination of the products solid substances are occasionally heated or fused in a glass tube closed at one end, thus resembling a small test-tube. It is made from a piece of straight glass tubing about 12 to 15 cm. in length and

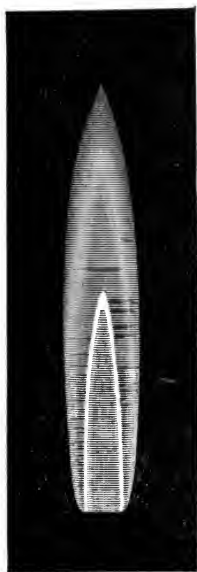


FIG. 8.—The flame of the Bunsen burner showing the four zones.

with a bore of about 4 mm. If this is heated in the middle until it is thoroughly softened, turning continually, it can be drawn apart while in the flame into two such tubes. The long point can be removed by touching it while red hot with another piece of glass. It should be used for only one fusion.

The flame of the Bunsen burner is not only a valuable agent as a heat-producer, but also for the production of chemical changes. If the holes below are closed so that no air enters, the flame is luminous but smoky, depositing a coating of unburned carbon or soot upon a cold object held in it. The temperature is then not very high because of the incomplete combustion. As air is admitted the yellow color disappears and the flame becomes blue. There is an increase in tempera-

ture and objects heated are not smoked. An examination shows this flame to be composed of several parts. (a) At the base, within, is a blue cone varying in height with the amount of gas. This is a mixture of air and gas which is not being burned. If a splinter is thrust into it and held there it will burn off at the margin of the flame before the ignition of the inner end occurs. (b) This cone is outlined by a line of lighter

blue. Here combustion is proceeding but not complete, there being present unburned carbon compounds of the gas. Under these conditions they will reduce oxygen compounds, that is, remove the oxygen from them (reduction or deoxidation). This part of the flame is called the reducing or deoxidizing zone. A copper wire oxidized by holding it above the flame until it is black will lose its oxygen and its dark color after it is held a few seconds in it. (c) Outside the zone of reduction lies a wider zone, the hottest part of the flame, since in it combustion is complete. It is called the zone of fusion and should be used when heat alone is desired. (d) The outer margin of the flame is bluish-white and rather indistinct. There the air is in excess and it is consequently able to oxidize, or give oxygen to, metals or other substances heated in it. It is called, therefore, the zone of oxidation or oxidizing zone.

In a similar manner the mouth blowpipe is made use of in effecting chemical changes. It is merely a bent tube of metal with a small opening through which air can be blown into a flame and the action of the latter can be thereby modified. The flame to be used is the yellow one made by closing the holes of the Bunsen burner or by slipping into it a smaller tube with a narrow opening above. This



FIG. 9.—The oxidizing flame produced with the blowpipe (color, light blue).

latter is preferable since less gas will be necessary and the flame can be better directed. To obtain an oxidizing action the yellow flame should be about 5 cm. high (2 inches) and, with the tip of the blowpipe just within the flame, enough air should be used to make it blue, directing the blast through the greatest diameter of the flame. With the blowpipe also the blue flame should be employed when great heat is desired. For the reducing flame perhaps

50 per cent. more gas should be used; the blowpipe should be held outside the flame and only enough air be forced in to make the flame horizontal, not sufficient to change the yellow



FIG. 10.—The reducing flame produced by the blowpipe (color, yellow).

color to a blue. The reducing action is due here as in the Bunsen-burner flame to the incompletely oxidized hot carbon.

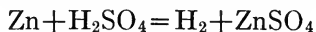
Chemical Reagents

Since chemical action proceeds more readily between dissolved compounds than solids, the reagents are in most cases used in solution. Unless for some particular reason large amounts of these, and concentrated solutions, should be avoided. The dilute acids, as a rule, give better results than the concentrated. When the latter are required such directions will be given. In separating two or more metals an "excess" of the reagent must be used, but this does not imply an excessively large volume or weight. It means merely enough to do the work for which it is added. If this is precipitation enough must be used to completely remove the precipitable elements and the solution must afterward be tested with more of the reagent to make sure that this has been done. If it is to acidify or make alkaline a solution the reagent should be slowly poured in and, after mixing, tests should be made to determine whether the liquid has the proper reaction.

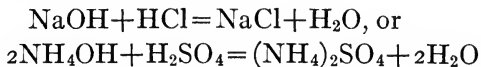
The reaction of a solution or other substance is ascertained

by its effect upon colored compounds, the one most commonly in use being litmus-paper—that is paper colored blue, red or purple with a vegetable coloring matter—litmus. If the liquid turns this red it is said to have an acid reaction; if it turns blue the reaction is alkaline. It is possible to make use of other colored substances besides this and a number will be so used in this course of study. The bases which are soluble in water change the color of red litmus to blue, or are alkaline in reaction; the insoluble bases do not affect the color.

Soluble acids redden litmus-paper, but an acid reaction in a liquid does not necessarily prove that a free acid is present, for other compounds can produce the same result. An acid is a compound of hydrogen with one or more negative (non-metallic) elements; and in the acids the hydrogen can be displaced by metals or similar substances and thus form a salt.



Salts are therefore seen to be composed of a metal or a similar substance united with the negative part of an acid. They can also be formed by the action of an acid upon a base, which latter consists of a metal, or a group of elements of similar properties, combined with OH. In such cases water is produced at the same time.



The Theory of Solution (Ionic Theory)

A knowledge of many chemical changes, including a majority of those of qualitative analysis, is facilitated by a knowledge of the ionic theory, a brief outline of which is given here. According to this theory, in aqueous solutions such are commonly used in analytical chemistry, acids, bases, and salts undergo a partial decomposition into their positive and negative com-

ponents, which are then called ions. This change is known as dissociation or ionization. The degree of ionization increases with the dilution, but varies for different compounds, being greater for strong acids and bases, or salts of these, than for the weak ones. The ions differ from the chemical elements in that they do not separate from the solution in such a way as to be visible. They may be composed of a single form of matter such as the ions of H or Cl from hydrochloric acid, or they may contain two or more forms of matter, such as NH_4 of ammonium salts or $\text{C}_2\text{H}_3\text{O}_2$ of acetic acid. All electrolytes, as compounds are called whose solutions conduct the electric current, are ionizable. The ions of a solution are set in motion if an electric current is passed through it and are named from the electrodes toward which they travel, cations going in the direction of the cathode or negative, and anions toward the anode or positive electrode.

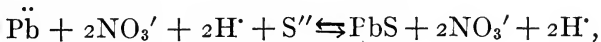
Under these conditions the ions can be considered as carriers of electricity. The univalent ones have a single charge and those of higher valence have electric charges proportional to the valence, the nature and amount being indicated by signs, such as Na^+ , Ba^{++} , Al^{+++} , Cl^- , NO_3^- , PO_4^{--} . Instead of the plus and minus signs these charges are often indicated by dots and dashes, as Na^{\cdot} , $\text{SO}_4^{''}$, etc. When these signs are present it means that the substances are not in the form of elements, but of ions. Thus the properties of H and H $^{\cdot}$, of Cl and Cl $^{\cdot}$, of S and S $^{''}$, are entirely different. When the ion loses its electric charge it becomes an element or group of elements.

The properties of dilute aqueous solutions are largely those of their ions; for example, the taste and action upon litmus of acids and bases seem to be due to the H $^{\cdot}$ and OH $^{\cdot}$ which are the constant constituents of these compounds, respectively. Dilute sulphuric acid contains H $^{\cdot}$ and $\text{SO}_4^{''}$ and has among its characteristic properties the evolution of hydrogen when brought in contact with zinc. The concentrated sulphuric

acid is practically not ionized and does not thus react with zinc.

The result of bringing together two solutions of ionized molecules will depend upon the nature of the substances which can be formed by rearrangement of the ions. Anything which permanently removes ions from the field tends to permanent chemical change. Thus in solutions of KOH and HCl we have $K^+ + OH^-$ and $H^+ + Cl^-$. It is possible for the H^+ to unite with OH^- to form water and, as the water is but extremely slightly ionizable, the change must be a permanent one—these substances cannot return to the ionic form. The same thing is true if they can unite to form a gas or an insoluble compound, since in this way the ionic materials leave the solution, that is, cannot be ionized again.

Cases of partial removal of ions by conversion into insoluble compounds are numerous. For example, in solutions of lead nitrate and hydrogen sulphid we find the ions $Pb^{++} + 2NO_3^-$ and $2H^+ + S^{--}$. But since PbS is an insoluble compound it is permanently formed as soon as the ions can react. If, however, we increase the nitric acid, precipitation is incomplete and can be prevented, or even the reaction be reversed, the PbS dissolving when sufficient H^+ is present. Such a reaction is reversible and can be represented by



indicating that the change can proceed in either direction, according to the relative amounts of H^+ or S^{--} present. This is an illustration of "mass action," the effect of increasing the mass, or amount, of one or other of the reacting substances. According to the law of mass action, the chemical action of two substances upon each other is proportional to the active mass of each. When no excessive quantity of either is present an equilibrium may be attained and neither change be complete.

It has been experimentally discovered that in a saturated

solution containing an ionized compound the product of the concentration of the ions divided by the concentration of the non-ionized molecules is a constant quantity. This can be represented, for instance, in the case of sodium chlorid, by

$$\frac{\text{concentration of Na}^+ \times \text{concentration of Cl}^-}{\text{Concentration of NaCl}} = \text{a constant.}$$

Experiment shows also that the ionization of a compound is lessened if to its solution is added either ion of the compound. For example, the ionization of sodium chlorid is decreased if hydrochloric acid is added, the Cl^- of the HCl being the effective agent. If the concentration of the original NaCl solution was sufficiently great, so that the union of Na^+ and Cl^- to NaCl produced more of the salt than the water can hold in solution a precipitate of NaCl will result.

Or, representing this phenomenon in another way by reference to the above fraction, if the Cl^- in the numerator increases (since the value of the fraction remains constant), either the concentration of the Na^+ must correspondingly decrease or the denominator, which represents the concentration of the non-ionized salt, must increase. If this latter change produces more salt than can be dissolved there is an immediate precipitation. On the other hand, a decrease of Na^+ can only be attained by union with the chlorin of the added HCl ; but the NaCl thus formed would result in the same precipitation as before.

The product of concentrations of ions spoken of above is called the solubility product.

Hydrolysis

As a rule, when chemical change takes place in an aqueous solution, the water is but very slightly ionized. However, if there is present a salt formed from a weak acid and a strong base or the opposite, the ions from the water may unite with the anion or the cation of the salt. For example, ferric chlorid, FeCl_3 , turns litmus red because the Fe^{+++} unites with the OH^- of the slightly ionized water to form Fe(OH)_3 leaving Cl^- with H^+ from the water and the H^+ gives the acid reaction. Again,

Na_2CO_3 in solution turns litmus blue; the hydrogen ion of the water unites with the CO_3'' to form HCO_3' thus leaving OH' which reacts alkaline (page 18). Such a change involving a decomposition of water is termed hydrolysis.

Oxidation and Reduction

Beside those changes where oxygen is removed from or added to a substance, chemists sometimes speak of reduction or oxidation where other negative elements, like chlorine, are so removed or added, thereby decreasing or increasing the valence of the positive element. With some of these the reaction occurs when the dry substances are heated or triturated together. With others the change is effected in solution, either by the aid of heat or at the ordinary temperature. An increase of positive valence in solution means an increase in the positive charge of the ion; hence oxidation may be defined as an increase in the positive charge and reduction as a decrease in the charge. It may take place suddenly or may require a long time for its completion. When the oxidizing agent is in the solid form the union may go on so rapidly as to cause a dangerous explosion. The production of either an oxidation or a reduction when medical substances are prescribed together is one form of incompatibility.

Incompatibility

An incompatibility in a prescription is caused by such a selection or combination of the components that the usual action of these is modified or prevented and undesirable results follow. The incompatibility may be a pharmaceutical one, where there is a physical but no chemical change, such as the separation of soluble matters from their solution. A therapeutical incompatibility occurs where drugs are prescribed together which are antagonistic in their physiological action upon the system. The third class, or chemical incompatibility,

is the only one with which this work will deal. In this the ingredients of the prescription act upon each other in such way as to produce a chemical change. It may not be a visible one, both or all resulting compounds remaining in solution; or, as is true in most instances, it may be perceptible. Some of the most common examples are those produced by the action of oxidizing agents which act both in dry mixtures, when explosions often occur, and in liquids. They are also caused by reducing agents, and in addition by those which without oxidation or reduction form insoluble substances or gases. In this manner the nature of the mixture may be entirely changed, perhaps being rendered inert on account of lessened absorption through its insolubility or, on the other hand, made more active or even poisonous through the formation of new compounds or by collecting the active principles in a precipitate which is taken with the last doses in the bottle. At times the incompatibility in a prescription is intentional, one of the ingredients being designed to precipitate another, such as the combination of lime-water and mercuric chlorid in the preparation of yellow wash. This, however, is infrequent. Many, although of course not all, of the chemical incompatibilities of medical compounds are illustrated by the reactions performed in the course of qualitative analysis. A thorough study should be made of these for the purpose of discovering such as are common or possible.

Where one or the other of the compounds entering into a reaction is a poison, the results obtained in the following tests may often be used in the selection of an antidote. This may act by forming an insoluble compound with the poison and thereby preventing its absorption, by forming an inert compound through union, or by more complete decomposition of the poisonous substance. Only a knowledge of their chemical properties will give the physician a mastery over the subject of poisons.

PART I

QUALITATIVE ANALYSIS

CHAPTER I

METALS (CATIONS)

THE PREPARATION OF SOLUTIONS FOR ANALYSIS

IN dissolving solids for analysis no general rule can be given except that the weakest possible solvent should be employed, and of that only as much as is necessary. Heat is generally of great assistance in effecting solution. It is advisable first to learn the best solvent by testing small amounts of the solid, and, when this has been ascertained, to use as much as is desirable for the analysis. Solvents may be tried in a test-tube in the following order, always warming the liquid, and using separate portions of solid for each test.

1. Water.
2. Dilute hydrochloric acid.
3. Concentrated hydrochloric acid (2-4 c.c.). Warm gently, afterward dilute with water and boil.
4. Nitric acid, first dilute, then concentrated.
5. The residue from 3 in dilute, then concentrated nitric acid.
6. Aqua regia.

If concentrated acid is necessary it should be largely removed, by evaporating nearly to dryness under a hood, before proceeding to the analysis. If the solid dissolves in two separate solvents, the solutions may be mixed for the analysis, provided this does not cause precipitation; or the portions may be tested separately.

Some substances which remain insoluble after the above treatment are the sulphates of barium, strontium, lead, and possibly calcium; the chlorid, bromid, iodid, and cyanid of silver; the oxids of tin, aluminum, chromium, silicon, and possibly iron; calcium fluorid; some silicates; carbon and sulphur. The residue can be fused on platinum with three times as much dry sodium carbonate, the mass boiled in water, filtered, and the filtrate tested for anions. Wash the residue, dissolve in dilute nitric acid and test for cations.

GROUP V

The Metals of the Alkalies, Potassium, Sodium (and Ammonium)

Almost all compounds of this group of metals are soluble in water, consequently they can rarely be identified by the formation of precipitates. Their hydroxids, carbonates, and also sulphids when dissolved in water are alkaline in reaction.

Potassium, K

Use a 5-per cent. solution of KCl for the following reactions.

1. Dip a looped platinum wire into a potassium solution and hold it in the outer part of a Bunsen flame. The color of the flame above the substance becomes bluish-violet. Look at the flame through one or more thicknesses of blue glass; (cobalt glass). The color is not destroyed by the glass, but becomes a more distinct violet. No other metal will give these results, although many organic compounds give a luminous flame which appears of a similar color through the blue glass. The organic matter may be first destroyed by burning and then the residue tested for potassium.

2. When a solution of sodium cobaltinitrite is added to one of potassium, the potassium ion unites with the cobaltinitrite ion, $\text{Co}(\text{NO}_2)_6'''$, to form a yellow precipitate of potassium

cobaltinitrite, $K_3Co(NO_2)_6$, which is somewhat soluble in water, and therefore may not appear except from rather concentrated solutions.

3. Platinic chlorid, to which hydrochloric acid has been added, contains the chlorplatinat ion, $PtCl_6''$ and precipitates the potassium ion from neutral or alkaline solutions, if they are not too dilute, in yellow octahedral crystals of potassium chlorplatinat, K_2PtCl_6 . The addition of alcohol renders the precipitation more complete.

Sodium, Na

Use a 5-per-cent. solution of NaCl for the test.

4. Compounds of sodium give an intense yellow color to the flame when volatilized in it, as in the potassium tests, on a platinum wire. This color does not pass through a blue glass providing the latter is of sufficient thickness.

Ammonium, NH_4

Use a 5-per-cent. solution of NH_4Cl for the reactions.

5. When ammonium salts, either solid or in solution, are heated with sodium hydroxid, NaOH, they are decomposed, ammonia, NH_3 , being liberated.



This is identified by its characteristic odor and also by its turning blue a moistened piece of red litmus-paper suspended in the mouth of the test-tube in such a manner that it does not touch the inside of the tube. The hydroxids of the alkaline earths and also of potassium will likewise set ammonia free from its compounds.

The explanation of the evolution of NH_3 from solutions of the ammonium ion is that NaOH being a strong base is, in solution, largely ionized to Na^+ and OH^- . Since NH_4OH is a weak base, it ionizes but slightly and consequently forms

when NH_4 and OH' come together. Being very unstable at a high temperature, it is decomposed by heating.



6. The ammonium ion, like the potassium ion, forms a yellow precipitate $(\text{NH}_4)_3\text{Co}(\text{NO}_2)_6$, with the cobaltinitrite ion. It does not appear in very dilute solutions because of its solubility in water.

7. A platinic chlorid solution, containing the chlorplatinate ion, PtCl_6'' , precipitates from neutral or acid solutions of ammonium salts, when they are sufficiently concentrated, yellow octahedral crystals of ammonium chlorplatinate $(\text{NH}_4)_2\text{PtCl}_6$. It is similar to the corresponding potassium compound.

8. All dry ammonium compounds are volatilized or decomposed when heated on platinum foil or a piece of porcelain.

9. A few drops of Nessler's reagent added to 10 c.c. of a solution of an ammonia compound gives a brown precipitate, NHg_2I . The test is so sensitive that one part of ammonia can be detected in a million of water. With such dilute solutions there is no precipitate, but only a yellow to brown color produced.

Practical Exercise in the Analysis of Group V

Mix in a test-tube 5 c.c.¹ each of solutions of potassium, sodium and ammonium. Warm half of this with sodium hydroxid and observe that ammonia is set free as from the simple solution. Make the flame test with the other half, observing the color both with and without the blue glass. The sodium yellow is seen without the glass and the potassium violet with it, neither interfering with the other.

¹ It is advisable that the student should, at the beginning of his course, determine the volumes of his test-tubes and other vessels in metric measures and thereafter use only these measures in chemical work.

Questions for Further Study on Group V

To be answered by the student.

How do you explain the destruction of the yellow light by the cobalt glass, while the violet passes through unchanged? What kind of chemical reagents turned red litmus blue? Why does the paper act more quickly if moist? Why should it not be allowed to touch the inner wall of the test-tube? Could the practical exercise above be used to determine the composition of an unknown mixture where K^+ , Na^+ and NH_4^+ might be present or absent? Can the dry sodium and potassium compound be freed from ammonium compounds by heating to a high temperature? What compounds of the alkali metals would be incompatible with acids? What would be the best for neutralizing acids? What property of a chemical compound prevents its appearance as a precipitate? What compounds of ammonium can be identified by the odor? Which of the compounds of the alkali metals are suitable for internal use as antidotes in case of poisoning by the mineral acids?

GROUP IV

The Metals of the Alkaline Earths, Magnesium, Calcium, Strontium and Barium

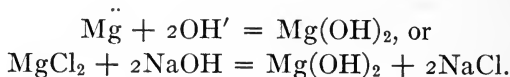
Their oxides are soluble in water (Mg only slight so), and the solution has an alkaline reaction. The phosphates and carbonates are insoluble in water, but soluble in acids, except those of barium, strontium, and calcium in sulphuric, the carbonate yielding CO_2 and neutralizing the acid. None of them form insoluble compounds by the action of hydrogen sulphid or ammonium sulphid.

Take for each test 3-4 c.c. of the solution of their salts.

Magnesium, Mg

Use a 5-per-cent. solution of $MgCl_2$ or $MgSO_4$ for the reactions.

10. The hydroxid ion (for instance from solutions of NaOH, KOH, NH_4OH , or $\text{Ba}(\text{OH})_2$) forms, with the magnesium ion, magnesium hydroxid, $\text{Mg}(\text{OH})_2$, a white gelatinous precipitate.



If NH_4OH is the reagent the precipitation is incomplete because complex soluble ammonium-magnesium ions are formed.

This precipitation does not occur if to the solution has been added an ammonium salt since, as has been shown (page 20), the common ion, NH_4 , so far decreases the ionization of the NH_4OH that the product of the concentration of the magnesium ion and the hydroxid ion is less than the solubility value. In all such cases no precipitate forms.

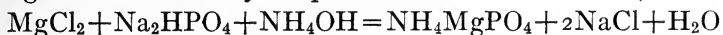
11. The carbonate ion, found conveniently in solutions of ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$, or sodium carbonate, Na_2CO_3 , produces basic carbonates varying in composition, types of which are MgCO_3 , $\text{Mg}(\text{OH})_2$, and $(\text{NH}_4)_2\text{Mg}(\text{CO}_3)_2$. Like the magnesium hydroxid, these carbonates are soluble in solutions of ammonium salts. They will therefore disappear upon the addition of ammonium chlorid to the liquid which contains them after heating, or, if ammonium chlorid is added to the magnesium solution before the carbonate ion, there is no precipitation.

These precipitates are very light, becoming heavier when heated in the liquid in which they are formed.

12. The phosphate or hydrophosphate ion, HPO_4'' , contained in a solution of sodium phosphate, Na_2HPO_4 converts the magnesium ion into insoluble, white MgHPO_4 . If ammonium hydroxid is present also the ammonium ion unites to form white crystalline ammonium magnesium phosphate, NH_4MgPO_4 . Some ammonium salt, like ammonium chlorid, should be added in order to prevent the union of the mag-

nesium and hydroxide ions and the consequent formation of magnesium hydroxide instead of the phosphate (10).

$\text{Mg} + \text{HPO}_4'' + \text{NH}_4' + \text{OH}' = \text{NH}_4\text{MgPO}_4 + \text{H}_2\text{O}$ or, representing all the original compounds and the products which might be obtained by evaporation from the solution,



Under the microscope the crystals are seen to have a stellate or fern-leaf form, especially if quickly precipitated. When formed slowly they are prismatic. All precipitates of magnesium are soluble in acids.

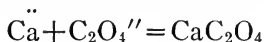
Calcium, Ca

Use for reactions a 5-per-cent. solution of CaCl_2 .

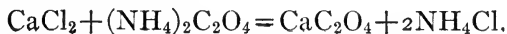
13. Calcium salts when held in the blue Bunsen flame give it a yellowish-red color. This is destroyed by the blue glass, through a thin piece of which it appears grayish-green. The flame test is most marked with the chloride or, when other salts are tested, after moistening with hydrochloric acid.

14. The carbonate ion, from such solutions as ammonium carbonate, precipitates the calcium ion as calcium carbonate, CaCO_3 , white and amorphous, and practically insoluble in ammonium salts. If, after settling, the solution is separated from the precipitate, the latter will dissolve with effervescence when an acid is poured on it.

15. The oxalate ion of the ammonium oxalate solution produces a fine, white precipitate of calcium oxalate, CaC_2O_4 from neutral or alkaline calcium solutions.



or, representing all the elements present except the solvent, water,



It is soluble in hydrochloric or nitric acid.

16. The sulphate ion, from a solution of dilute sulphuric acid or any sulphate except that of calcium, precipitates from a concentrated solution, fine, white, calcium sulphate, CaSO_4 , which is soluble in a large amount of water. It is, in consequence, not precipitated from dilute solutions. The calcium ion cannot be precipitated by a solution of calcium sulphate.

17. The phosphate ion throws down from calcium solutions a white, flocculent acid calcium phosphate, CaHPO_4 .

18. The dichromate ion does not precipitate the calcium ion.

Strontium, Sr

A 5-per-cent. solution of SrCl_2 may be used for the reactions.

19. Strontium salts give a deep crimson color to the blue flame, best after the addition of hydrochloric acid. This is seen through a thin blue glass but not through a thick one.

20. The carbonate ion gives a white, flocculent precipitate of SrCO_3 , similar in properties to CaCO_3 .

21. The oxalate ion precipitates strontium oxalate, SrC_2O_4 , if the solution is not very dilute. It is a fine white powder.

22. The sulphate ion precipitates strontium as the sulphate, SrSO_4 . The strontium sulphate is somewhat soluble in water, consequently it is not completely precipitated and appears rather slowly in dilute solutions. It is less soluble in alcohol.

23. The phosphate ion produces a white, flocculent precipitate of SrHPO_4 , acid strontium phosphate.

24. The dichromate ion does not precipitate strontium from its neutral or acid solutions.

Barium, Ba

All soluble barium compounds act as poisons.

Use for the reactions a 5-per-cent. solution of BaCl_2 .

25. Barium chlorid and most other barium salts to which

hydrochloric acid has been added produce a yellowish-green flame when held in the oxidizing flame of a Bunsen burner.

26. The carbonate ion precipitates barium from its solution as BaCO_3 , similar in its properties to the carbonates of calcium and strontium.

27. The oxalate ion forms barium oxalate, BaC_2O_4 , a fine, white, heavy precipitate.

28. The sulphate ion precipitates immediately the barium from its solution as a heavy, very fine, white solid—barium sulphate, BaSO_4 .

29. The phosphate ion yields barium phosphate, BaHPO_4 , a compound similar in composition, formation and properties to the corresponding salts of calcium and strontium.

30. The dichromate ion or the chromate ion from the solutions of potassium dichromate (bichromate), or potassium chromate precipitates bright yellow barium chromate, BaCrO_4 , insoluble in acetic acid.

Directions for the Separation of the Cations of Groups IV and V

If the solution which contains the ions of groups IV and V is not already alkaline make it so by adding a little ammonium hydroxid, then about 5 c.c. of ammonium chlorid and, finally, ammonium carbonate as long as a precipitate is formed. Warm nearly to the boiling-point and filter. Wash the precipitate, discarding the wash-water.

The precipitate contains the carbonate of barium, strontium, and calcium. The filtrate contains magnesium, potassium, and sodium.

Dissolve the precipitate on the paper by pouring over it 5-10 c.c. of hot acetic acid, using the same acid repeatedly if the first application is insufficient. To the resulting solution add potassium dichromate which precipitates the barium as

yellow barium chromate. Filter and, after diluting the filtrate with water to about 25 c.c., add dilute sulphuric acid to precipitate the strontium. The precipitate of strontium sulphate is a very fine white solid. Let it settle five minutes. Filter, wash, moisten the precipitate on the filter with a few drops of hydrochloric acid and confirm the presence of strontium by the deep crimson color imparted to the flame of a Bunsen burner when the substance is held in it on a platinum wire. It is also reddish through thin cobalt glass. Make the filtrate from the strontium alkaline with ammonium hydroxid, then add ammonium oxalate. Calcium is precipitated as fine, white calcium oxalate. It may be confirmed by the reddish-yellow color of its flame, testing in the same manner as for strontium. It appears a dirty green through a thin blue glass.

The solution containing magnesium, potassium, and sodium should be tested first for the sodium and potassium by the color imparted to a Bunsen-burner flame—yellow from sodium, and violet when potassium is present and the flame is viewed through a sufficiently thick blue glass. The test is more delicate, with small amounts of these metals, if the liquid is first concentrated to a few cubic centimeters by boiling.

To detect magnesium add to the solution which has been tested for sodium and potassium a little sodium phosphate. Shake vigorously and let it stand without warming. Magnesium ammonium phosphate is precipitated—small, white snowflake-shaped crystals when seen with the microscope. An excess of ammonium hydroxid favors the precipitation.

The presence of ammonium in the original substance can be determined only by applying the test to this directly. This is done by adding 5 c.c. of sodium hydroxid, or enough to give an alkaline reaction, and boiling. The ammonia gas which is evolved can be identified by its characteristic odor or by its turning red litmus-paper blue.

TABLE I

OUTLINE OF SEPARATION OF CATIONS OF GROUPS IV AND V

Heat a small portion of the original substance with sodium hydroxid. An evolution of ammonia gas indicates ammonium.

Make the remainder of the solution which contains groups IV and V alkaline with ammonium hydroxid and add ammonium chlorid and ammonium carbonate, heat, filter, and wash.

Precipitate contains BaCO_3 , SrCO_3 , CaCO_3 . Dissolve in dilute acetic acid and add potassium dichromate. Filter.		Filtrate contains Mg, K and Na. Test color of flame. Yellow indicates Na. Violet through the blue glass indicates K. Add sodium phosphate. A white, crystalline precipitate indicates Mg.	
A yellow precipitate is BaCrO_4 .	Solution contains Sr and Ca. Add dilute H_2SO_4 .		
	A fine white precipitate is SrSO_4 . Confirm by crimson flame.	Solution contains Ca. Make alkaline with ammonium hydroxid and add ammonium oxalate. A fine white precipitate is CaC_2O_4 . Confirm by reddish-yellow flame.	

Explanations of the Operations Used in the Separation of the Cations of Groups IV and V

The ammonium chlorid must be used here to prevent the precipitation of magnesium with the others of the alkaline earth metals (10). Ammonium hydroxid is necessary to neutralize any acid that may be present as this would decompose the ammonium carbonate and prevent the precipitation of any of the ions. The carbonates of barium, strontium, and calcium which are formed in cold solutions are not completely precipitated if carbon dioxid is present because of the formation of soluble acid carbonates, but these are converted by heating into insoluble ones.

The acetic acid displaces the carbonic acid from the precipitated carbonates, the positive part of the compounds going into solution as cations. The majority of precipitates are not soluble with sufficient ease to allow this method of

solution, but must be removed from the filter and mixed, or often heated, with the solvent. The effervescence is caused by the evolution of CO_2 which is always set free by the action of an acid on a carbonate. If no water were added to the solution of strontium and calcium before the former was precipitated as a sulphate some or most of the calcium might also be thrown down (16). Strontium is slowly precipitated on account of the solubility of its sulphate (22), therefore, it is necessary to allow sufficient time for this to be accomplished.

If the strontium sulphate were not washed some of the calcium solution would remain, if this metal were present in the mixture, and the color of the flame would be modified. The acid makes it more distinct.

Ammonium oxalate does not precipitate bases of this group from acid solutions, such as this one is after the use of sulphuric acid, consequently the latter must be neutralized in order to detect the calcium.

The flame test for the alkalis should not be made until the removal of the barium, strontium, and calcium ions from the mixture because of the effect they would give if they were present. The sodium would not be concealed, but the potassium might be difficult of identification (19).

The test for sodium must be applied before that for magnesium because the precipitation of magnesium requires a sodium salt and the sodium from this remains in solution and passes into the filtrate from the magnesium. With solid sodium compounds or very concentrated solutions some of the light may pass through the cobalt glass if this is not sufficiently thick, but it then appears blue, and not violet, as can be seen by comparing it with a known potassium solution.

The sodium phosphate precipitates the magnesium very completely, but if there is not much magnesium present a long time of standing may be necessary.

The original substance can be tested for ammonium by

adding sodium hydroxid to it directly without dissolving as the ammonia will be readily set free. If only a minute amount is present it can be detected by hanging the moist red litmus-paper, in such a manner that it shall not touch the tube, from a cork which closes the test-tube and allowing it to stand for twenty-four hours at the ordinary temperature. The test with litmus-paper is much more sensitive than identification by the odor. In this case care must be taken that the reagent contains no ammonium compounds. It is necessary to use the original substance to test for ammonia and not the filtrate from barium, strontium and calcium carbonates where we might naturally look for it, since before getting this filtrate a number of ammonium compounds have been added to the solution.

Practical Exercises in the Separation of the Cations of Groups IV and V

Mix in a large test-tube 3-4 c.c. of the solution of each and analyze the mixture of the seven according to Table I.

In the same manner make analyses of unknown mixtures of these groups, which can be obtained from the instructors, and report results in writing.

Questions for Further Study on Group IV

Why are the metals of group IV called metals of the alkaline earths? When their oxids dissolve in water is there any chemical change? What is such a solution of calcium called? For what is it used? What property of these compounds is made use of to separate the cations of this group from those of group V? What is meant by effervescence? Why might it be expected that the flame of calcium compounds would be more plain by the addition of hydrochloric acid? What would be the effect of adding alcohol to a mixture of sulphuric acid with a dilute solution of strontium? Why does not a

solution of calcium sulphate precipitate concentrated solutions of calcium salts when this can be done by the use of other soluble sulphates? Why will an ammonium oxalate solution not precipitate calcium from a strongly acid solution? In the analysis of group IV what would be indicated, if instead of a crystalline precipitate where we should expect magnesium, a white amorphous precipitate should appear? Are there any other alkaline gases except ammonia? Which compounds of the metals of group IV can be employed for the neutralization of acids? Are any ever used medicinally for this purpose? Can an acid be neutralized by a substance which is itself neutral in reaction? What use is made of calcium carbonate in medicine? By what other name is magnesium carbonate known, and for what properties is it valuable in medicine? What is the difference in composition between the soluble acid carbonate of calcium and the insoluble carbonate of the same metal? Where does the former occur naturally?

GROUP III

Aluminum, Chromium, Zinc, Manganese, Cobalt, Nickel and Iron

Not only the carbonates and phosphates of this group are insoluble in water, but also the oxids, hydroxids, and sulphids, except the sulphids and carbonates of aluminum and chromium which cannot be formed by precipitation but are hydrolyzed to the hydroxids. The ions of the group are therefore precipitated from neutral solutions by hydroxid, carbonate, phosphate, and sulphid ions, the carbonate and sulphid ions forming hydroxids of aluminum and chromium by hydrolysis. Hydrogen sulphid does not precipitate ions of this group from acid solutions.

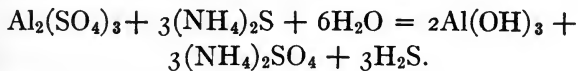
Aluminum (Aluminium), Al

Aluminum dissolves in hydrochloric acid and caustic alkalis, but only slowly in other acids. Aluminum acts as a cation, Al^{+++} , also as part of an anion like AlO_2' or AlO''' .

Use for the reactions of the cation a 5-per-cent. solution of $\text{Al}_2(\text{SO}_4)_3$ or $\text{KAl}(\text{SO}_4)_2$.

31. The sulphid ion, which can be obtained from a solution of ammonium sulphid, produces in solutions of the cation a very light, gelatinous, white precipitate of aluminum hydroxid, $\text{Al}(\text{OH})_3$.

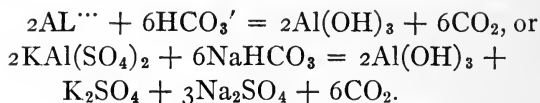
Aluminum sulphid, the formation of which might be expected, cannot exist in water, but hydrolyzes (page 20), yielding the hydroxid and hydrogen sulphid, $\text{Al}_2\text{S}_3 + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 + 3\text{H}_2\text{S}$. Hydrogen sulphid produces no precipitate with the aluminum ion unless the H^+ is neutralized by adding the hydroxid ion, for example, from NH_4OH or NaOH . Aluminum hydroxid is readily soluble in acids.



32. When barium carbonate, suspended in water, is mixed with an aluminum solution the liquid, after filtration or settling of the residue, will be found free from aluminum.

33. The hydroxid ion precipitates the cation, Al^{+++} , as the hydroxid, $\text{Al}(\text{OH})_3$, described in 31. This dissolves immediately in an excess of the reagent, if sodium hydroxid or potassium hydroxid has been used, the aluminum then being found in the anion, as NaAlO_2 , sodium aluminate. If the reagent is ammonium hydroxid the aluminum hydroxid is but slightly soluble and can be completely precipitated by heating. With sodium hydroxid or potassium hydroxid the aluminate formed is not decomposed by heating and the hydroxid does not precipitate on boiling. It can be precipitated by adding ammonium chlorid, best by the aid of heat. Acidifying the solution of the aluminate destroys it, leaving the aluminum as the cation.

34. The carbonate ion with solutions of the aluminum ion (cation) likewise forms aluminum hydroxid, hydrolysis occurring as with the sulphid, and CO_2 escaping.



Chromium, Cr

Chromium may be met with in two classes of compounds the salts, where it occupies the positive part of the compound, forming the cation in solutions, such as CrCl_3 or $\text{Cr}_2(\text{SO}_4)_3$; and the chromates, or chromic acid derivatives, where it is found in the negative part, such as PbCrO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$. With these two classes most reagents give different results. Only the former will be considered in this place.

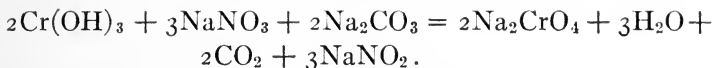
The chromic salts have a green or violet color, the chromic ion is also green.

Use for the reactions of the chromic salts a 5-per-cent. solution of $\text{KCr}(\text{SO}_4)_2$.

35. The sulphid ion (from ammonium sulphid) precipitates the chromic ion as chromium hydroxid, $\text{Cr}(\text{OH})_3$, a grayish-green or bluish-green, voluminous gelatinous compound. It is soluble in acids. Hydrogen sulphid is formed by hydrolysis as it is by the action of ammonium sulphid on aluminum salts.

36. The hydroxid ion precipitates the chromic ion as chromium hydroxid. It is soluble in excess of the reagent, imparting a pink or green color to the liquid, but is precipitated from this solution as chromic hydroxid by boiling.

37. Dry compounds of chromium if mixed with dry potassium or sodium nitrate and sodium carbonate and then fused on the platinum foil are thereby converted to yellow potassium or sodium chromates. These are soluble in water, forming a bright yellow liquid and giving the reactions of chromic acid. Thus, after acidifying with acetic acid, a drop of lead acetate solution gives a yellow precipitate of lead chromate, PbCrO_4 . For this test any of the precipitates may be employed after filtering from the solution and drying on the foil



38. Barium carbonate precipitates basic chromium salts in the same manner as it does those of aluminum.

Zinc, Zn

Zinc is readily soluble in hydrochloric, nitric, and sulphuric acids. Its salts are colorless.

For the reactions a 2-per-cent. solution of ZnSO_4 may be used.

39. The sulphid ion, obtained best from ammonium sulphid, precipitates the zinc ion, from its neutral or alkaline solutions as the sulphid, ZnS . It is a white flocculent solid, insoluble in excess of the reagent or in alkalies, but soluble in most mineral acids. With hydrogen sulphid the precipitation is incomplete.

40. The hydroxid ion precipitates zinc hydroxid, $\text{Zn}(\text{OH})_2$, a white gelatinous compound readily soluble in excess of ammonia. On boiling the zinc hydroxid precipitates again in whole or in part unless ammonium salts are present, which will prevent the separation. From solutions in sodium hydroxid or potassium hydroxid it does not precipitate on boiling, if a large excess of the alkali is present.

41. The ferrocyanid ion (potassium ferrocyanid) precipitates zinc ferrocyanid, $\text{Zn}_2\text{Fe}(\text{CN})_6$, a white compound, insoluble in cold dilute hydrochloric acid but somewhat soluble in an excess of the reagent.

Manganese, Mn

Metallic manganese dissolves easily in acids with the formation of the manganous ion, Mn^{++} . Manganese is also found in the manganate ion, MnO''_4 , which is green, and the permanganate ion, MnO'_4 , which is purple.

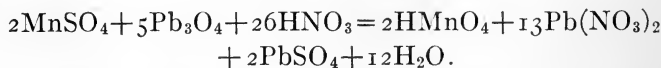
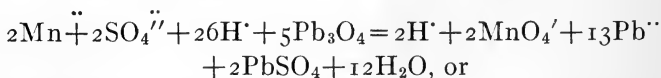
Use for the reactions of the manganous ion a 2-per-cent. solution of MnSO_4 .

42. The sulphid ion (from ammonium sulphid) precipitates the manganous ion as the sulphid, MnS , a flesh-colored compound which upon standing exposed to the air becomes dark brown. This precipitate is insoluble in excess of the reagent, but dissolves readily in acids.

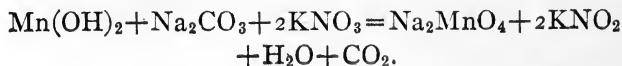
43. The hydroxid ion produces a precipitate of manganous hydroxid, $\text{Mn}(\text{OH})_2$, which is at first nearly white, but when shaken in the tube with air, or allowed to stand exposed to it, becomes quickly dark brown from the absorption of oxygen and the formation of manganic hydroxid, $\text{Mn}(\text{OH})_3$. The precipitate is insoluble in excess of sodium hydroxid but dissolves in acids.

If ammonium hydroxid is used the precipitation is prevented by the presence of ammonium chlorid.

44. If as much Pb_3O_4 (red lead) as can be held on the point of a pen-knife is added to a solution of the manganous ion and if the mixture is then strongly acidified with nitric acid, boiled and allowed to settle, the liquid above has a red color due to the formation of the permanganate ion. The presence of hydrochloric acid or chlorin compounds interferes with, or prevents, the reaction.



45. Solid compounds of manganese when mixed with several times their weight of dry sodium carbonate and potassium nitrate and fused on the platinum foil become converted to green sodium manganate, Na_2MnO_4 , the color of which is best seen while it is melted.



If too much of the manganese compound is used the mass may be black. In the cold it dissolves in water to a green solution. This is decomposed by boiling the liquid, the manganese being precipitated as an oxid. The green solution gradually changed to a pink through exposure to the air, the manganate ion being converted to a permanganate ion, MnO_4' .

Iron, Fe

The metal is soluble in hydrochloric, sulphuric, and nitric acids. There are two series of compounds, the ferrous and the ferric. The former are, for the most part, colorless or greenish and unite with oxygen when brought in contact with oxidizing agents, or even when exposed to the air, especially in the presence of water. They are thus converted into ferric compounds which are usually yellowish to reddish-brown.

Ferrous Ion (Fe'')

For the reactions use a 2-per-cent. solution of FeSO_4 .

46. The sulphid ion from ammonium sulphid precipitates the ferrous ion completely from neutral or alkaline solutions as black ferrous sulphid, FeS . This dissolves in dilute acids and oxidizes in the air to brown ferric hydroxid.

47. The hydroxid ion produces ferrous hydroxid $\text{Fe}(\text{OH})_2$. If the ferrous solution is pure and oxygen is excluded from that and the reagent the color at first is nearly white. Without these special precautions, however, it is a grayish-green which soon changes by oxidation to a darker green and finally is converted to reddish-brown ferric hydroxid, $\text{Fe}(\text{OH})_3$. This precipitation is prevented by the presence of many non-volatile organic acids or their salts and by ammonium salts; also by other organic compounds like sugar and glycerin.

48. The ferrocyanid ion, $\text{Fe}(\text{CN})_6'''$, (potassium ferrocyanid), with the ferrous ion which is free from the ferric ion gives a bluish-white precipitate of potassium ferrous ferrocyanid, $\text{K}_2\text{FeFe}(\text{CN})_6$. This becomes deep blue by the

action of the oxygen of the air or by oxidizing agents. Hydroxids of the alkalis destroy the blue color.

49. The ferricyanid ion, $\text{Fe}(\text{CN})_6'''$, with a ferrous solution produces a deep blue precipitate of ferrous ferricyanid, $\text{Fe}_3\text{-Fe}_2(\text{CN})_{12}$. Hydroxids of the alkalis decompose this. With very dilute solutions of iron salts the last two reagents produce only a greenish color.

50. The sulphocyanate ion, SCN' , imparts no color to ferrous solutions if they do not contain ferric compounds.

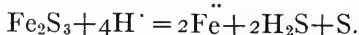
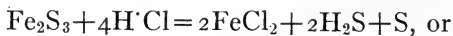
51. The carbonate ion precipitates the ferrous ion as white ferrous carbonate, FeCO_3 , which, when moist, rapidly oxidizes in air, giving up its CO_2 , ferric hydroxid, $\text{Fe}(\text{OH})_3$, being formed.

52. Tannic or gallic acids produce no color with ferrous solutions if they are free from ferric salts.

The Ferric Ion (Fe'')

For the reactions use a 2-per-cent. solution of FeCl_3 .

53. The sulphid ion in alkaline solution, *e.g.*, from ammonium sulphid, precipitates the ferric ion as black ferric sulphid, Fe_2S_3 . This, for the most part, decomposes upon acidifying, with reduction of the iron to the ferrous condition and precipitation of sulphur.



54. The hydroxid ion precipitates the ferric ion as ferric hydroxid, $\text{Fe}(\text{OH})_3$, a reddish-brown, gelatinous substance. It cannot be thus formed in solutions containing a large amount of non-volatile organic acids, sugar or glycerin. It dissolves readily in acids, but is insoluble in excess of the precipitant and in solutions of ammonium salts.

Inasmuch as in an ionic change the number of positive and negative charges lost must be equal, when the ferric ion loses six of the positive the sulphur ion must lose the same number of negative charges. Since but four would be lost from the two

sulphur ions which unite to form the insoluble ferrous sulphid the loss of two more negative charges causes a change of a sulphur ion to the elementary form, that is, the sulphur precipitates. At the same time the ion has changed from the ferric to the ferrous form, that is, reduction has occurred.

55. The ferrocyanid ion with ferric solutions gives a dark blue precipitate of ferric ferrocyanid, $\text{Fe}_4\text{Fe}_3(\text{CN})_{18}$ —"Prussian blue." This is insoluble in hydrochloric acid, but is decomposed by the alkaline hydroxids with the separation of ferric hydroxid, similarly to the decomposition of ferrous ferrocyanid.

56. The ferricyanid ion changes the color of ferric solutions to a brown, but does not form a precipitate.

57. The sulphocyanate ion gives with the acidified ferric ion a deep blood-red color without forming a precipitate. The color is due to the formation of non-ionized ferric sulphocyanate, $\text{Fe}(\text{SCN})_3$. An excess of the sulphocyanate ion intensifies the color by decreasing the ionization of the compound (p. 20). Hydrochloric acid does not decolorize it. The reaction may be used as an extremely sensitive test for iron. When soluble phosphates, borates or some organic acids are present the reaction may fail until the solution is strongly acidified with hydrochloric acid. The color is destroyed by the addition of mercuric chlorid.

58. The carbonate ion precipitates from ferric solutions reddish-brown, gelatinous ferric hydroxid, $\text{Fe}(\text{OH})_3$, CO_2 escaping.

59. Barium carbonate precipitates ferric compounds completely in the cold as basic salts.

60. Tannic or gallic acid forms a blue-black precipitate with ferric solutions.

Nickel, Ni

Nickel dissolves slowly in hydrochloric and in dilute sulphuric acids, more readily in nitric acid. Nickelous salts of

these acids are then formed. Most of the solutions of nickel are green, the color of the nickel ion.

A 2-per-cent. solution of NiSO_4 may be used for the reactions.

61. The sulphid ion from ammonium sulphid in neutral or alkaline solutions precipitates black nickel sulphid, NiS , slightly soluble in excess of the reagent, in the presence of ammonium hydroxid, to a brownish solution. It does not dissolve in cold dilute hydrochloric acid, but dissolves in aqua regia.

62. The hydroxid ion gives at first a greenish precipitate of nickelous hydroxid, Ni(OH)_2 , which dissolves to a blue liquid in a slight excess of ammonium hydroxid, through the formation of a complex ion of nickel and ammonia, but does not in excess of sodium or potassium hydroxid.

63. With sugar and some ions of organic acids, like tartaric, the nickel ion enters into combinations with which the hydroxid ion or the sulphid ion forms no precipitate. Thus, if a solution of sodium potassium tartrate (Rochelle salt) is added to Ni and the mixture is then made strongly alkaline with NaOH addition of the sulphid ion does not precipitate NiS , but gives a brown solution.

64. Potassium nitrite does not precipitate nickel from its solution in acetic acid.

Cobalt, Co

Cobalt, like nickel, dissolves in acids, with the formation of cobaltous salts. These are usually pink to red when they contain water of crystallization and blue when anhydrous. The dilute solutions are red also, the color of the cobaltous ion.

Use a 2-per-cent. solution of $\text{Co(NO}_3)_2$ in the reactions.

65. The sulphid ion, from ammonium sulphid, precipitates the cobalt ion from neutral or alkaline solutions as the black sulphid, CoS . It is insoluble in excess and in cold hydrochloric acid but dissolves, like the nickel sulphid, in aqua regia.

Tartrates do not prevent the precipitation of CoS from alkaline solutions as they do of NiS.

66. The hydroxid ion gives a precipitate of a blue basic salt. It dissolves in excess of the ammonia, with the formation of a complex cobalt-ammonium ion, to a pink solution if the liquid is freed from oxygen and this, on standing in the air, becomes brown from oxidation. Organic compounds may prevent the precipitation.

67. Upon boiling with an excess of sodium hydroxid or potassium hydroxid the blue basic salt is converted into pink insoluble cobaltous hydroxid, $\text{Co}(\text{OH})_2$.

68. A solution of cobalt when made strongly acid with acetic acid, after the addition of a considerable amount of potassium nitrite and standing for several hours in a warm place, will give a yellow, crystalline precipitate of potassium cobaltic nitrite, $\text{K}_3\text{Co}(\text{NO}_2)_3$.

The cobaltous ion, Co^{++} , is converted into the cobaltic, Co^{+++} , by oxidizing agents, *e.g.*, nitrous acid which is set free through the decomposition of the nitrite by the acetic acid. The complex ion $\text{Co}(\text{NO}_2)_3^{+++}$ is thus formed, the potassium salt of which is insoluble.

Directions for the Separation of Cations of Group III in the Absence of Phosphoric, Oxalic, Boric, Citric, and Tartaric Acids

The acidity of the solution containing the group should be neutralized by adding ammonium hydroxid slowly, until a permanent precipitate begins to form. Then add about one-tenth its volume of ammonium chlorid and last ammonium sulphid until complete precipitation has been produced, but avoiding a large excess. Heat the mixture nearly to boiling and filter. If the original mixture contained groups IV and V they will be found in the filtrate. Otherwise it can be discarded. The precipitate contains the sulphids of nickel,

cobalt, iron, manganese, and zinc, with the hydroxids of chromium and aluminum. Wash it with hot water.

Rinse the precipitate from the filter with about 15 c.c. of dilute hydrochloric acid and let it stand five minutes in the acid, stirring occasionally. All the members of the group with the exception of nickel and cobalt dissolve. ~~The nickel and~~ cobalt remain as black sulphids. If the insoluble residue is light colored or gray it may be only sulphur. Filter and wash.

Test the residue with the borax bead in the oxidizing flame. Cobalt gives a blue bead; nickel a purple, white hot, soon becoming brown. If the residue is so small that it cannot be removed from the paper, the part of the filter which contains it can be burned on the bead, when, after the complete oxidation of the carbon, the metal will be left to dissolve in the borax.

When only one of the two is present the colors will be clear but if both are contained in the bead, it may be necessary to separate them before they can be identified.

One method to accomplish this is to dissolve the mixed sulphids in 2 c.c. of warm aqua regia, filter and evaporate nearly to dryness under a hood, to remove the excess of acid. Dilute with water to 5 c.c., add potassium nitrite and acidify strongly with acetic acid; warm gently and let it stand several hours. The cobalt gives a yellow precipitate. Filter and test the filtrate for nickel by sodium hydroxid or ammonium sulphid. The former gives a green precipitate; the latter, a black one.

As an alternate method of separation of cobalt and nickel, after dissolving the sulphids in 1 c.c. of hydrochloric acid with 0.5 c.c. of nitric acid add a solution of Rochelle salt; make alkaline with ammonium hydroxid and add an excess of ammonium sulphid; black cobalt sulphid is precipitated; nickel remains dissolved as a brown compound, seen after filtration.

Boil, for a short time, the hydrochloric acid solution of iron,

manganese, chromium, aluminum, and zinc until it is freed from hydrogen sulphid as shown by the absence of odor or by its failure to discolor a paper dipped in lead acetate and held in the steam. Add to the hot liquid bromin water until it is colored yellow and bring to a boil. Make it alkaline with sodium hydroxid, then add enough of the sodium hydroxid to make a large excess.¹ Boil one minute and filter. The iron, manganese, and chromium are precipitated as hydroxids, and the zinc and aluminum are dissolved in the excess of the alkali. Dissolve a small portion of the precipitate in hydrochloric acid and test it for iron with potassium ferrocyanid. A blue color is produced. Place another portion of the precipitate on the platinum foil, add five times as much of a mixture of dry sodium carbonate and potassium nitrate and heat until it is thoroughly fused. If manganese is present the mass is a deep green. Chromium, in the absence of manganese, gives a yellow mass. In either case, to confirm the presence of chromium place the foil in a test-tube, cover with water and heat to boiling. Filter off the brownish residue, if one is present, and test the solution for chromium, after acidifying with acetic acid, by adding a few drops of lead acetate. A yellow precipitate of lead chromate is produced.

The solution of aluminum and zinc in excess of sodium hydroxid should be slightly acidified with hydrochloric acid, then an excess of ammonium hydroxid should be added and the liquid boiled for several minutes. Aluminum hydroxid, a very flocculent white precipitate, is produced, which floats a long time in the liquid. Filter and, after dividing the filtrate into two parts, test one for zinc by a few drops of ammonium sulphid and warming. A flocculent white precipitate appears. From the second part, after it has been acidified with hydrochloric acid, potassium ferrocyanid precipitates zinc ferrocyanid, a very fine, white solid.

¹ When sufficient alkali has been added the liquid has a soapy feeling if a drop is rubbed between the fingers.

TABLE II

① OUTLINE OF SEPARATION OF THE CATIONS OF GROUP III IN ABSENCE OF PHOSPHORIC, BORIC, ETC., ACIDS

To the solution add NH_4OH until, after shaking, there is a slight permanent precipitate. Then add NH_4Cl and a slight excess of $(\text{NH}_4)_2\text{S}$. Warm, filter, and wash. The precipitate contains NiS , CoS , FeS (or Fe_2S_3), MnS , ZnS , $\text{Cr}(\text{OH})_3$, and $\text{Al}(\text{OH})_3$ if they were present in the original solution. Let it stand five minutes in cold dilute HCl , stirring frequently. All are dissolved except the sulphids of Ni and Co . Filter and wash.

② If the insoluble residue is black apply the borax bead test.

A blue bead = Co .

A brown bead = Ni .

If a separation of the metals is desired dissolve the black residue in a little aqua regia, evaporate nearly to dryness, dilute with 5 c.c. of water, add KNO_3 , acidify with acetic acid and let it stand several hours, after warming. A yellow precipitate of potassium cobalt nitrite is formed. Filter and to the filtrate add NaOH and warm. $\text{Ni}(\text{OH})_2$ a light green precipitate appears. With the same filtrate $(\text{NH}_4)_2\text{S}$ gives a black precipitate, NiS .

Or, add excess of NaOH to aqua regia solution, then a tartrate and $(\text{NH}_4)_2\text{S}$. Ni gives a brown solution; Co , a black precipitate.

③ The filtrate contains Fe , Mn , Zn , Cr , and Al ions.

Expel the hydrogen sulphid by boiling and add a slight excess of bromin water.

Then heat to boiling, make the liquid very strongly alkaline with NaOH , and boil one minute. Filter.

④ The precipitate contains $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, and $\text{Mn}(\text{OH})_2$.

Dissolve a small portion of the precipitate in HCl and test for Fe with $\text{K}_4\text{Fe}(\text{CN})_6$. A dark blue color should appear.

Dry another portion of the precipitate on platinum foil, and thoroughly fuse with Na_2CO_3 and KNO_3 .

Dark green K_2MnO_4 is formed.

Boil with a little water, filter, acidify with acetic acid and add lead acetate. Yellow PbCrO_4 is precipitated.

⑤ The filtrate contains Al and Zn .

Slightly acidify it with HCl , make it alkaline with NH_4OH and boil a minute. A light white precipitate is $\text{Al}(\text{OH})_3$.

Filter and test the filtrate for Zn .

1. $(\text{NH}_4)_2\text{S}$ gives a white flocculent precipitate, ZnS .

2. $\text{K}_4\text{Fe}(\text{CN})_6$ gives a fine white precipitate of $\text{Zn}_2\text{Fe}(\text{CN})_6$ after acidifying with HCl .

Explanation of the Operations Used in the Separation of the Cations of Group III

The object of the addition of ammonium hydroxid is to neutralize any acid present, since this would otherwise decompose the ammonium sulphid and prevent the precipitation of the cations. Ammonium chlorid favors the complete precipi-

tation of many of these, converting the products from a gelatinous to a more or less flaky consistency, which hastens the subsequent filtration. Warming likewise favors the precipitation and rapid filtration of the group. The precipitation should be accomplished chiefly by the ammonium sulphid, a large excess of which, together with ammonium hydroxid may cause a partial solution of the nickel sulphid. This gives the filtrate a brown color.

By the action of the hydrochloric acid the compounds of all the metals, with the exception of nickel and cobalt, are converted to chlorids which are soluble. The sulphids of these two metals are not soluble in cold dilute acid, although they are somewhat so if it is heated or in the concentrated acid. Sulphur is set free from the ammonium sulphid by the action of ferric salts (53).

When the sulphids of the metals are dissolved in the acid hydrogen sulphid is formed, and remains dissolved in the cold liquid. If it is not removed it would, as soon as the liquid becomes alkaline in the next operation, change the iron, manganese, and zinc compounds again into the sulphids instead of the hydroxids. The zinc would remain with them, instead of being separated by the sodium hydroxid.

Bromin water and other oxidizing agents change ferrous compounds to ferric in the presence of free acid. After this has been added it is necessary to use a large excess of the sodium hydroxid, since by a small amount all five of the cations in the solution would be precipitated.

The fusion of the hydroxids of iron, manganese, and chromium does not change the appearance of the iron compound, but converts the manganese into a green manganate which is changed by boiling into an insoluble oxid (45). At the same time the chromium hydroxid is oxidized to a soluble yellow chromate (37).

If the aluminum solution is not made acid the aluminum

will not be precipitated by ammonium hydroxid even if large amounts are present (33).

Separation of the Cations of Groups III and IV in the Presence of Phosphoric Acid or its Salts

(Capital and small letters are used for the identification of subdivisions of the groups—the former for solids, the latter for solutions)

The cations of group III and IV are ordinarily precipitated separately from those of group V. If, however, the solution contains certain acids or their salts the cations of both groups are thrown down together by the reagents used for the precipitation of group III. If it has been ascertained by testing that phosphates are present, the usual separation of the cations of groups III and IV should be modified in the following manner:

To the solution of the two groups add about one-tenth its volume of ammonium chlorid, make it faintly alkaline with ammonium hydroxid and then add ammonium sulphid until no more precipitate (*A*) forms. Warm and stir the mixture until the precipitate begins to settle, filter and wash with water containing a few drops of $(\text{NH}_4)_2\text{S}$. Preserve the filtrate to test for cations of group IV which may be partially unprecipitated. The precipitate (*A*) may contain all the metals of groups III and IV, together with some of V and sulphur. Rinse it from the paper with about 15 c.c. of dilute hydrochloric acid into a dish or beaker and stir it occasionally for five minutes. Filter and wash. There will remain insoluble (*B*) the sulphids of cobalt and nickel with sulphur. The remaining compounds are dissolved and passed into the filtrate (*a*).

Nickel and cobalt sulphids, if present, are black; sulphur is grayish to yellow, burning with characteristic odor and blue flame is present in large quantity. To test for the nickel or cobalt dissolve the residue (*B*) in a borax bead with the aid of

the oxidizing flame. Cobalt gives a deep blue color; nickel, a purple while hot, quickly passing to a brown. In cases of doubt or where it is desirable to separate the metals, dissolve it in aqua regia and use potassium nitrite or tartrate as on page 46.

The hydrochloric acid solution (*a*) is to be used for the separation of the remaining cations. Boil it in a beaker or flask until the hydrogen sulphid is expelled, as shown by the absence of odor and by the failure of a strip of filter-paper to turn brown after it has been moistened with lead acetate solution and suspended in the steam. If much sulphur separates during this boiling filter it out.

Mix about one-fourth of the solution (*a*) with dilute sulphuric acid. The sulphate of barium will be immediately precipitated (*C*), that of strontium, if much is present, or upon standing, and of calcium if this is present in concentrated solution, although the calcium in great part remains dissolved. After it has settled filter and wash, preserving the filtrate (*b*). If there is no precipitation by sulphuric acid calcium may nevertheless be in solution. To detect it here or after filtration from the sulphates of barium and strontium add three volumes of alcohol to (*b*) when the calcium sulphate will be precipitated if present. It can be dissolved in boiling water and tested with a few drops of ammonium oxalate which should give a fine white precipitate of calcium oxalate. To test for barium and strontium if sulphuric acid caused a precipitation place the washed, moist precipitate (*C*) in a porcelain dish, add about 10 c.c. of a 10-per-cent. solution of sodium carbonate, and boil gently for five minutes. Strontium sulphate, and calcium sulphate if it is present, are converted into carbonates, the barium sulphate being but little affected. Filter and wash. Pour over the precipitate (*D*) on the filter 10 c.c. of hot acetic acid which will dissolve (*c*) the strontium carbonate, but comparatively little of the

barium salt. Wash the precipitate (*D*), discarding the wash-water. The barium may be confirmed by the appearance of a yellow-green flame obtained from the insoluble residue (*D*) after it has been moistened with hydrochloric acid. To the acetic acid solution (*c*) add a few drops of potassium dichromate to precipitate the barium if any of this has been dissolved. This will be changed to yellow barium chromate. Filter when enough of the reagent has been added to give the supernatant liquid a yellow color. From the filtrate (*d*) precipitate the strontium by means of dilute sulphuric acid, adding it as long as the insoluble compound is formed and letting the mixture stand five minutes if no precipitate appears immediately. Filter and, after washing, confirm the strontium by moistening with hydrochloric acid and making the flame test with and without the blue glass (19).

To about a cubic centimeter of the hydrochloric acid solution (*a*) add enough bromin water to give a yellow color, boil and add a few drops of potassium ferrocyanid. A blue color is indicative of iron.

To the remainder of the hydrochloric acid solution (*a*), if iron has been found, add bromin water and boil as before. If iron is absent omit this step and proceed with the next operation, which is to remove from the solution (*a*) the phosphoric acid that may be present. This is effected by forming an insoluble compound of this with iron. To learn whether enough iron is present in the solution remove two or three drops and to these, in an evaporating dish, add ammonium hydroxid. If there is a yellowish-brown precipitate the amount of iron is sufficient; if it is nearly white add to the solution a few drops of ferric chlorid, and test a little of this with ammonium hydroxid as before, repeating as many times as necessary to produce the yellow or brown precipitate. The free acid should now be nearly but not quite neutralized. This must be done by dropping in, with constant stirring,

sodium hydroxid solution until blue litmus-paper is only slowly turned red. If too much has been used hydrochloric acid must be added until the proper reaction is attained. Now add an excess of barium carbonate. This is best done by shaking the solid reagent with water and using the milky mixture. Let this stand in the cold for half an hour, with frequent stirring. The liquid above the precipitate should be colorless if enough has been used. Then filter and wash. The precipitate (*E*) contains the hydroxids of aluminum, chromium, and iron, also the ferric phosphate and the excess of the barium carbonate. The filtrate (*e*) will contain the manganese and zinc, also the barium, strontium, calcium, and magnesium, which may have been contained in the original substance.

Transfer the precipitate (*E*) from the filter to a porcelain dish, then boil it two minutes with about 10 c.c. of sodium hydroxid, cool and filter. This dissolves the aluminum, which passes into the filtrate. From this it can be precipitated by first acidifying with hydrochloric acid, then making faintly alkaline with ammonium hydroxid and boiling for a minute in a beaker. The aluminum hydroxid thus obtained is a white, very voluminous substance, which floats for a long time in the liquid.

To detect the chromium in the portion of the barium carbonate precipitate (*E*) which did not dissolve in sodium hydroxid, dry it on platinum foil, then fuse thoroughly with a mixture of dry sodium carbonate and potassium nitrate. The chromium produces a yellow mass which dissolves to a yellow solution in water, and this, after acidifying with acetic acid, forms a bright yellow, insoluble lead chromate upon the addition of lead acetate.

To test for magnesium, zinc, and manganese proceed as follows with the filtrate (*e*) from the barium carbonate precipitate. Acidify with dilute sulphuric acid, heating until

the effervescence has ceased. This precipitates the barium, most of the strontium, and possibly part of the calcium, and dissolves the manganese, zinc, and magnesium. Filter and neglect the precipitate, since the bases contained in it have already been determined. To the filtrate add ammonium hydroxid until it is alkaline, then ammonium sulphid. Manganese and zinc are precipitated (*F*) as sulphids if they were contained in the mixture. Magnesium, with calcium and possibly some strontium, remains in the liquid (*f*). Filter and wash. Remove the precipitate (*F*) from the paper, dissolve it in a slight excess of hydrochloric acid, free it from hydrogen sulphid by boiling in an evaporating dish, and make it strongly alkaline with sodium hydroxid. White manganous hydroxid, soon turning brown, is precipitated, the zinc remaining in solution (*g*). Confirm the manganese by fusing it on the platinum foil with sodium carbonate and potassium nitrate, when a dark green mass results. The zinc may be separated from the solution (*g*) in sodium hydroxid by the aid of a little hydrogen sulphid, which gives a white flaky precipitate of zinc sulphid.

To determine whether any magnesium is contained in the solution (*f*) from which the manganese and zinc sulphids have been filtered, add ammonium oxalate which may give a white precipitate of calcium or strontium oxalate. Remove this by filtration if it is formed and to the filtrate add ammonium hydroxid and sodium phosphate. A white crystalline precipitate indicates magnesium.

TABLE III

OUTLINE OF SEPARATION OF THE CATIONS OF GROUPS III AND IV

In the presence of phosphoric acid or its salts. To the solution add NH_4Cl , make alkaline with NH_4OH and precipitate with $(\text{NH}_4)_2\text{S}$. Warm, filter, and wash. The precipitate contains NiS , CoS , FeS (or Fe_2S_3), MnS , ZnS , $\text{Al}(\text{OH})_3$, and $\text{Cr}(\text{OH})_3$, with Ba , Sr , Ca , and Mg salts of phosphoric acid, sometimes with S . Treat with HCl . If a residue remains, filter and wash.

<p>If the residue is black it may contain CoS and NiS. Test it with borax bead. A blue bead indicates Co, a brown bead indicates Ni. To separate or distinguish these dissolve in aqua regia and use KNO_2 or Rochelle salt as on page 46.</p>	<p>The filtrate contains Fe, Mn, Cr, Al, Zn, Ba, Sr, Ca, and Mg. Expel the H_2S by boiling and divide the solution into three portions. To the first add dilute H_2SO_4. Filter and wash.</p> <p>Precipitate contains BaSO_4 and SrSO_4 with possibly CaSO_4. Boil with Na_2CO_3, filter and wash. Insoluble residue contains BaSO_4 ($\text{BaCO}_3?$), SrCO_3 ($\text{CaCO}_3?$). Treat with acetic acid. Insoluble BaSO_4 remains. Confirm with flame test. From solution precipitate Ba with $\text{K}_2\text{Cr}_2\text{O}_7$, filter and add H_2SO_4; white precipitate of SrSO_4. Filter, wash, and confirm by crimson flame.</p>	<p>Filtrate contains Fe, Mn, Cr, Al, Zn, Ca, and Mg. Test a portion for Fe by $\text{K}_4\text{Fe}(\text{CN})_6$. If iron is present, after oxidizing this with Br water add enough FeCl_3 to unite with the phosphoric acid, nearly neutralize the acidity and add BaCO_3. Allow to stand one-half hour. Then filter and wash.</p>			
		<table> <tr> <td data-bbox="440 697 574 1246"> <p>Precipitate contains $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, and $\text{Al}(\text{OH})_3$. Boil with NaOH and filter.</p> <p>Residue contains $\text{Cr}(\text{OH})_3$. Fuse with Na_2CO_3 and KNO_3. Dissolve in water, add acetic acid and lead acetate. A yellow precipitate of PbCrO_4.</p> </td><td data-bbox="574 697 709 1121"> <p>Filtrate contains Al. Acidify with HCl, add NH_4OH and boil. A light white precipitate of $\text{Al}(\text{OH})_3$.</p> </td><td data-bbox="709 697 1033 1494"> <p>Filtrate contains Mn, Zn, $\text{Ca}(\text{Sr}?)$, and Mg. Acidify with dilute H_2SO_4 and filter out the Ba and Sr if there is a precipitate. In the filtrate precipitate the Mn and Zn with NH_4OH and $(\text{NH}_4)_2\text{S}$. Filter.</p> <p>Precipitate contains MnS and ZnS. Dissolve in HCl. Expel H_2S by boiling and add large excess of NaOH. $\text{Mn}(\text{OH})_2$ is precipitated. Confirm by fusion with Na_2CO_3 and KNO_3 on Pt foil. Mn gives a green mass. From filtrate precipitate white, flaky ZnS by H_2S.</p> <p>Filtrate contains (Ba, Sr?) Ca and Mg. With $(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitate all except Mg and remove by filtration. To the filtrate add Na_2HPO_4. Mg gives a white crystalline precipitate of NH_4MgPO_4.</p> </td></tr> </table>	<p>Precipitate contains $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, and $\text{Al}(\text{OH})_3$. Boil with NaOH and filter.</p> <p>Residue contains $\text{Cr}(\text{OH})_3$. Fuse with Na_2CO_3 and KNO_3. Dissolve in water, add acetic acid and lead acetate. A yellow precipitate of PbCrO_4.</p>	<p>Filtrate contains Al. Acidify with HCl, add NH_4OH and boil. A light white precipitate of $\text{Al}(\text{OH})_3$.</p>	<p>Filtrate contains Mn, Zn, $\text{Ca}(\text{Sr}?)$, and Mg. Acidify with dilute H_2SO_4 and filter out the Ba and Sr if there is a precipitate. In the filtrate precipitate the Mn and Zn with NH_4OH and $(\text{NH}_4)_2\text{S}$. Filter.</p> <p>Precipitate contains MnS and ZnS. Dissolve in HCl. Expel H_2S by boiling and add large excess of NaOH. $\text{Mn}(\text{OH})_2$ is precipitated. Confirm by fusion with Na_2CO_3 and KNO_3 on Pt foil. Mn gives a green mass. From filtrate precipitate white, flaky ZnS by H_2S.</p> <p>Filtrate contains (Ba, Sr?) Ca and Mg. With $(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitate all except Mg and remove by filtration. To the filtrate add Na_2HPO_4. Mg gives a white crystalline precipitate of NH_4MgPO_4.</p>
<p>Precipitate contains $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, and $\text{Al}(\text{OH})_3$. Boil with NaOH and filter.</p> <p>Residue contains $\text{Cr}(\text{OH})_3$. Fuse with Na_2CO_3 and KNO_3. Dissolve in water, add acetic acid and lead acetate. A yellow precipitate of PbCrO_4.</p>	<p>Filtrate contains Al. Acidify with HCl, add NH_4OH and boil. A light white precipitate of $\text{Al}(\text{OH})_3$.</p>	<p>Filtrate contains Mn, Zn, $\text{Ca}(\text{Sr}?)$, and Mg. Acidify with dilute H_2SO_4 and filter out the Ba and Sr if there is a precipitate. In the filtrate precipitate the Mn and Zn with NH_4OH and $(\text{NH}_4)_2\text{S}$. Filter.</p> <p>Precipitate contains MnS and ZnS. Dissolve in HCl. Expel H_2S by boiling and add large excess of NaOH. $\text{Mn}(\text{OH})_2$ is precipitated. Confirm by fusion with Na_2CO_3 and KNO_3 on Pt foil. Mn gives a green mass. From filtrate precipitate white, flaky ZnS by H_2S.</p> <p>Filtrate contains (Ba, Sr?) Ca and Mg. With $(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitate all except Mg and remove by filtration. To the filtrate add Na_2HPO_4. Mg gives a white crystalline precipitate of NH_4MgPO_4.</p>			

Explanation of the Operations Used in the Separation of the Cations of Groups III and IV in the Presence of Phosphoric Acid or its Salts

The reason that it is necessary to modify the usual methods when this acid is contained in the solution is that the phosphates of barium, strontium, calcium, and magnesium are soluble in acids, but not in neutral or alkaline liquids. They therefore will be precipitated with the third group as soon as ammonium hydroxid has been added. Many of the explanations given regarding the analysis of groups III and IV will also be applicable here.

Nickel and cobalt can be easily separated from the rest of the precipitated metals because of the insolubility of their sulphids in dilute acid. From the solution thus obtained all the barium and most of the strontium are separated by conversion into sulphates by means of sulphuric acid which dissolves the other compounds. This does not make a clean separation between the alkali earth metals, though, since a part of the strontium may be left in solution or a part of the calcium may be changed to the insoluble sulphate if a large amount is present. Nevertheless it serves to distinguish them from each other. To give greater certainty of this the flame test should not be neglected. In the same way when the sulphates of barium and strontium are boiled with sodium carbonate some of the barium sulphate may become converted to the carbonate as the strontium sulphate is and thus pass with the strontium into solution.

The separation of the metals contained in the sulphuric acid filtrate is the same as in the separation where the metals of the alkaline earths are not present, except that alcohol is used to render more insoluble the calcium sulphate, and after the metals of group III have been identified and the calcium

removed the magnesium is precipitated by sodium phosphate in the usual manner.

Practical Exercises on Group III

1. In a large test-tube mix together 3-4 c.c. of the solutions of each of the cations of the group and separate them according to Table II.

2. In the same manner make analyses of the unknown mixtures which will be furnished by the instructors.

3. To solutions of these metals add those of group IV and sodium phosphate and make the analysis by the directions in Table III.

4. Examine the unknowns furnished by the instructors to determine whether they contain phosphates. If this is the case analyze the mixture by Table III.

Questions for Further Study on Group III

In the fusion of chromium and manganese compounds with sodium carbonate and potassium nitrate what action has each of the latter reagents? What is the action of the Pb_3O_4 and nitric acid in the production of the red color from manganous compounds? Would ferrous or ferric salts be formed when iron is dissolved in hydrochloric acid? in dilute sulphuric acid? in concentrated nitric acid? Which will the more easily dissolve iron, concentrated or dilute sulphuric acid? What are some of the pharmaceutical preparations of iron from which ammonium hydroxid would fail to produce a precipitate? What is the valence of the iron in ferrocyanid and ferricyanid? For what is ferrous carbonate used in medicine and what means is then adopted to prevent its oxidation? Is the rapidity of oxidation of ferrous compounds modified by the presence or absence of moisture? What pharmaceutical preparations would be incompatible with iron compounds because of their containing tannic or gallic acid?

What compounds of the alkali metals are chemically incompatible with salts of this group because of the resulting insoluble compounds? What can be used to prevent this precipitation? What chemical reagents can be employed to convert ferrous into ferric compounds? What application is made of the mutual decomposition of alum and an alkaline carbonate.

GROUP II

Arsenic, antimony, tin, gold, platinum, mercury (ic compounds), lead, bismuth, copper, cadmium. The cations of this group are precipitated from their acid solutions by hydrogen sulphid. For convenience they may be divided into two divisions: (A) Those of which the sulphids are insoluble in yellow ammonium sulphid—mercuric compounds, lead, bismuth, copper, and cadmium, and (B) those of which the sulphids are soluble in yellow ammonium sulphid—arsenic, antimony, tin, gold, and platinum.

Division A

The sulphids of this division do not form soluble sulphosalts with the alkaline sulphids and are consequently insoluble in these reagents. Their oxides, hydroxides, carbonates, phosphates, arsenates, arsenites, and iodides as well as sulphids are insoluble in water.

Copper, Cu

The metal is practically insoluble in dilute sulphuric or hydrochloric acids, but dissolves readily in nitric acid. Its soluble compounds are poisonous.

For the reactions a 2-per-cent. solution of CuSO_4 may be used.

69. The sulphid ion gives a brownish, nearly black, precipitate of copper sulphid, CuS . It dissolves in hot nitric acid, also in solutions of potassium cyanid.

70. The hydroxid ion, with the copper ion, forms the light blue, insoluble, cupric hydroxid $\text{Cu}(\text{OH})_2$, which is insoluble in excess of sodium hydroxid or potassium hydroxid. It is decomposed by boiling into black cupric oxid, CuO , and water. The presence of some organic compounds like glycerin, sugar, and salts of tartaric and some other organic acids prevents the precipitation of the copper ion by the hydroxid ion, but instead it forms a deep blue solution. If one of the reducing sugars, like glucose, is present this, by boiling, reduces the cupric to a cuprous compound and yellow or reddish cuprous oxid is precipitated.

71. Ammonium hydroxid in small amounts forms with the copper ion a blue precipitate, but this dissolves easily in an excess of the reagent to a deep blue solution which contains the complex ion, $(\text{NH}_3)_4\text{Cu}$. The addition of potassium cyanid decolorizes the liquid.

72. The carbonate ion precipitates basic cupric carbonate which dissolves in excess of ammonium carbonate.

73. The ferrocyanid ion gives a precipitate of reddish-brown cupric ferrocyanid, $\text{Cu}_2\text{Fe}(\text{CN})_6$, insoluble in dilute acids.

74. Metallic iron or zinc precipitates reddish metallic copper which collects on the metal.

75. Cupric chlorid gives a light blue color to the Bunsen flame; most other copper compounds give an emerald-green.

Bismuth, Bi

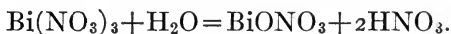
Bismuth will dissolve in nitric acid, forming the nitrate, and is not easily attacked by other acids. It is a weak base and its salts readily undergo hydrolysis, the bismuth being precipitated as a basic salt, and most of the acid being set free. Hence its solutions have an acid reaction, and free acid must be present to keep it dissolved.

Use for the reactions a 2-per-cent. solution of $\text{Bi}(\text{NO}_3)_3$.

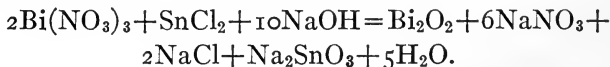
76. The sulphid ion precipitates black bismuth sulphid, Bi_2S_3 , soluble in nitric acid.

77. The hydroxid ion precipitates $\text{Bi}(\text{OH})_3$, a white bulky solid, insoluble in excess.

78. A bismuth solution, free from a large amount of nitric acid, after dilution with ten to twenty times its volume of water undergoes hydrolysis and a white precipitate is formed. Instead of the hydroxid which would be expected, the reaction is reversible and a basic salt is produced. Boiling or the addition of a few drops of hydrochloric acid favors the precipitation.

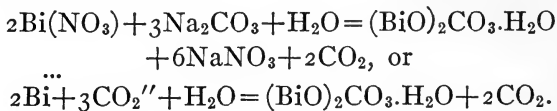


79. The stannous ion added to a solution of bismuth previously made alkaline by sodium hydroxid reduces the bismuth compound to the black oxid, Bi_2O_3 . This test can also be applied to many of the solid compounds.



80. The dichromate ion produces a yellow precipitate of bismuth oxychromate, $(\text{BiO})_2\text{CrO}_4$, which is soluble in nitric acid and insoluble in sodium hydroxid.

81. The carbonate ion precipitates white basic bismuth carbonate, or subcarbonate.



Cadmium, Cd

Cadmium dissolves in nitric, hydrochloric or dilute sulphuric acid with the formation of the corresponding salts.

A 2-per-cent. solution of $\text{Cd}(\text{NO}_3)_2$ may be used for the reactions.

82. The sulphid ion precipitates from cadmium solutions

bright-yellow cadmium sulphid, CdS , which dissolves in nitric acid but not in solutions of potassium cyanid or alkaline sulphids.

83. The hydroxid ion gives a precipitate of white cadmium hydroxid, $\text{Cd}(\text{OH})_2$, which is soluble in an excess of ammonium hydroxid.

84. The carbonate ion precipitates white cadmium carbonate, insoluble in excess.

Mercury

Mercury cannot be dissolved in hydrochloric acid. In cold, dilute nitric acid it dissolves to mercurous nitrate, HgNO_3 ; in hot, concentrated nitric acid it also dissolves, forming then mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$. Salts of mercury volatilize upon heating to a high temperature in the absence of water either without or with decomposition. All the soluble compounds are poisonous.

The Mercuric Ion, Hg^{++}

For the reactions a 2-per-cent. solution of $\text{Hg}(\text{NO}_3)_2$ or HgCl_2 may be employed.

85. The sulphid ion with mercuric solutions forms a white precipitate, if a very small amount of the reagent is used. As the reagent is increased the color changes to yellow; then brown and, finally, black, insoluble mercuric sulphid, HgS , is formed. This is insoluble in yellow ammonium sulphid, also in nitric or hydrochloric acids when used singly. It does, however, dissolve easily in aqua regia.

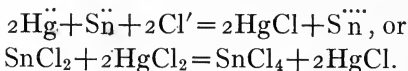
86. The hydroxid ion, if obtained from sodium hydroxid or potassium hydroxid, produces a yellow precipitate of mercuric oxid, HgO .

If ammonium hydroxid is used as the reagent the NH_3 present unites with the mercuric ion to form a complex ion,

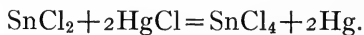
$\text{Hg}^{\ddot{}} + \text{NH}_3 = \text{H}^{\cdot} + \text{HgNH}_2^{\cdot}$. This with Cl' precipitates white mercuric aminochlorid, NH_2HgCl .



87. The addition of a slight amount of the stannous ion in the presence of HCl forms with the mercuric ion a white precipitate of mercurous chlorid, HgCl .

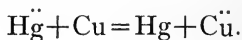


If more of the stannous ion is added the white precipitate is changed to gray metallic mercury which only very slowly collects into large globules.



Other reducing agents produce HgCl , or, if strong, gray mercury in a similar manner.

88. A strip of sheet copper in a solution of mercury acidified with hydrochloric acid (but free from nitric acid) precipitates the mercury as a gray film of the metal on the surface of the copper.



By rubbing with a cloth or the finger this becomes a bright, white copper amalgam. If the strip is inserted in a narrow test-tube and this is heated the mercury is volatilized and collects as a gray ring in the cool part of the tube. When examined with the microscope it is seen to be composed of globules of the metal. When these are rubbed with a glass rod they collect into larger globules. If a single crystal of iodine is dropped into the tube and this is then gently warmed the metal is converted into the bright scarlet iodid, HgI_2 . Zinc and iron, like copper, convert the mercury from the ionic to the elementary form.

89. The iodid ion with mercuric solutions forms a red pre-

precipitate of mercuric iodid, yellow at first but soon becoming scarlet. It is soluble in excess of either potassium iodid or mercuric chlorid.

90. Dry compounds of mercury if mixed with dry sodium carbonate and heated in a tube are decomposed, the mercury appearing in globules on the upper part of the glass.

91. Besides the above reagents many animal and vegetable substances form insoluble compounds with mercuric solutions, *e.g.*, albumin, alkaloids, extractive matter, and a great number of others.

Division B

The sulphids of this division unite with sulphids of the alkalies to form soluble compounds which are called sulpho- or thio-salts. These can be decomposed by acids, hydrogen sulphid being set free and the metals reprecipitated as sulphids.

Arsenic, As

Metallic arsenic is oxidized by dilute nitric acid to arsenous acid, and by concentrated nitric acid to arsenic acid, both of which are soluble. It is insoluble in hydrochloric and dilute sulphuric acids. Almost all its compounds are poisonous.

Dry Reactions of Arsenic and its Compounds

92. Metallic arsenic volatilizes when heated, giving a garlic odor. If the heating is done in a glass tube the metal is deposited upon the upper, cool part of the tube as a coating with a metallic luster. When in a rather thick layer it appears black by transmitted light, but it is of a brown shade when only a minute amount is present.

93. If a small fragment of the metal is placed in the middle of a narrow glass tube a few inches in length and open at both ends and is then heated over the Bunsen flame, holding the

tube obliquely, the arsenic is oxidized and the white crystalline As_2O_3 is deposited in the upper part.

94. Arsenous oxid As_2O_3 , if heated in a glass tube, sublimes without an odor, and is deposited upon the cooler part of the tube in octahedral or tetrahedral (eight-sided or four-sided) crystals. Their shape can be plainly seen with a microscope. The best crystals are obtained by having the upper part of the tube slightly warmed so as to prevent too rapid a deposition of the oxid.

95. Arsenous oxid when volatilized over glowing charcoal is reduced to the metal. This can be demonstrated by drawing out the closed end of a small tube to a rather narrow point and, after it has cooled, placing a fragment of the oxid in the end, with a splinter of charcoal above it. Heat the charcoal to redness first, then gradually heat the arsenic compound. A dark mirror of arsenic appears in the upper part of the tube. Some other compounds of arsenic will give the same result, but not all of them.

96. Arsenic sulphid and some of the arsenic compounds which are not reduced to the metallic form by charcoal alone, will be thus changed by mixing with sodium carbonate and potassium cyanid, both previously thoroughly dried, and heating in the tube. The mirror appears as before.

Reactions of Arsenic Ions

In making the reactions of the ions of arsenic we may consider them as belonging to two classes, first those in which the arsenic acts as the cation, as it does in the halogen compounds, and, secondly, the arsenous and arsenic acids and their salts (arsenites and arsenates) where the arsenic is found in the negative part or anion. Some reactions will be common to all compounds; others will give different results with the different classes.

97. Arsenous oxid is soluble in water, though with difficulty. When so dissolved it forms the weak acid, H_3AsO_3 , arsenous acid. It dissolves in hydrochloric acid to arsenous chlorid, AsCl_3 . Sodium hydroxid or potassium hydroxid dissolves arsenous oxid easily with the formation of the arsenites of these metals. Nitric acid and also aqua regia convert it into soluble arsenic acid, H_3AsO_4 .

General Reactions of the Arsenous Ion

Use a 1-per-cent. solution of AsCl_3 , As_2O_3 , or K_3AsO_3 .

98. The sulphid ion with neutral or alkaline solutions gives no precipitate, but upon the addition of hydrochloric acid it precipitates the arsenic as bright yellow arsenous sulphid, As_2S_3 . This is soluble in the alkaline hydroxids, carbonates, or sulphids, but not in hydrochloric acid. When it is dissolved in ammonium sulphid ammonium thioarsenite, or sulpharsenite is formed, NH_4AsS_2 . This is decomposed by acids, As_2S_3 being reprecipitated. Boiling nitric acid dissolves it after converting it into arsenic acid.

Reactions of the Arsenite Ion (Arsenous Acid and Arsenites)

Use a 1-per-cent. solution of As_2O_3 or K_3AsO_3 .

99. The silver ion in neutral solutions of an arsenite forms yellow silver arsenite, Ag_3AsO_3 , soluble both in excess of ammonia and of nitric acid. This reaction is concealed by the presence of any acid or salt which precipitates silver nitrate, such as hydrochloric acid or the chlorids. A convenient way to make the reaction is to first acidify the arsenous solution with nitric acid in a narrow test-tube, then, after adding a few drops of silver nitrate, to slant the tube and pour ammonium hydroxid down the side carefully so as to prevent the liquids from mixing. The precipitate appears in the neutral zone between them.

100. The copper ion in neutral solutions in the same way produces yellowish-green cupric arsenite, CuHAsO_3 . It dissolves in either ammonium hydroxid or nitric acid.

101. Cations of most metals except those of the alkalies form insoluble arsenites in neutral solutions.

General Reactions of the Arsenic Ion

Use a 1-per-cent. solution of Na_2HAsO_4 .

102. The sulphid ion gives no precipitate in neutral or alkaline solutions of arsenates. If they are acidified it slowly reduces them to arsenous compounds, then precipitates them as arsenous sulphid, As_2S_3 . Warming hastens the reduction and precipitation, but several hours are required for its completion—sometimes twenty-four. Sulphur is precipitated at the same time.

103. With the sulphid ion in an alkaline solution, or if ammonium sulphid is used, no precipitate is produced, although the soluble ammonium thioarsenate, $(\text{NH}_4)_3\text{AsS}_4$, is formed. When this is acidified with hydrochloric acid yellow arsenic sulphid, As_2S_5 , is precipitated.

Reactions of the Arsenate Ion (Arsenic Acid and Arsenates)

Use a 1-per-cent. solution of Na_2HAsO_4 .

104. The silver ion produces in neutral solutions of arsenates a reddish-brown precipitate of silver arsenate, Ag_3AsO_4 , soluble in dilute nitric acid and ammonium hydroxid. The reaction may be made in the same manner as in 99.

105. The copper ion precipitates from neutral solutions greenish-blue cupric arsenate, CuHAsO_4 , soluble in ammonium hydroxid or nitric acid.

106. Magnesia mixture (magnesium sulphate with ammonium chlorid and ammonium hydroxid; it must be a clear solution and not cloudy) forms white crystalline ammonium

magnesium arsenate with the arsenate ion. It dissolves easily in acids.

107. Cations of most metals except the alkali metals form, in neutral liquids, insoluble arsenates.

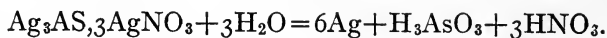
General Reactions of Arsenous and Arsenic Ions

Use a 1-per-cent. solution of any compound of arsenic.

108. From solutions of arsenic, strongly acidified with hydrochloric acid and warmed with strips of sheet copper, copper arsenid is precipitated which forms a dark-gray film on the surface of the copper. With very dilute solutions this can be accomplished by placing the solution with the copper in a test-tube and letting it stand half an hour in a beaker of boiling water. If then the copper is removed, washed with water, dried and heated in a small open tube (93) the arsenic is oxidized to As_2O_3 , which is deposited in microscopic crystals. The copper remains black from the formation of its oxid. This test (Reinsch's test) is very sensitive and is not prevented by the presence of organic matter.

109. Acidify 3-4 c.c. of arsenic solution with pure hydrochloric or sulphuric acid, add a small piece of zinc (about one gram) that is known to be free from arsenic, cover the mouth of the tube with several thicknesses of filter-paper upon the upper one of which has been put a drop of *saturated* silver solution. Let the tube stand where it is protected from a bright light and from hydrogen sulphid. After a time, varying with the amount of arsenic present, the spot on the paper becomes yellow with a brown or black margin. The addition of water changes it to black. The yellow compound is Ag_3As , 3AgNO_3 . This is produced by the action of the AsH_3 —formed by the nascent hydrogen with the soluble arsenic compound—and the silver nitrate. Water decomposes it, setting free metallic silver.

Gutzeit's test.



A mercuric chlorid solution can be substituted for the saturated silver nitrate and gives a yellow color also.

This test is a very sensitive one.

110. If sodium hydroxid or potassium hydroxid is substituted for the acid, the reaction being otherwise performed in the same way, except that the solution may be slightly warmed the same result appears (Fleitzmann's test). This reaction is of value in distinguishing between arsenic and antimony.

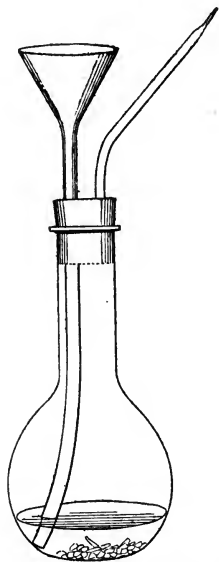


FIG. 11.—A simple form of generator for Marsh's test.

111. To 3–4 c.c. of an arsenic solution add an equal volume of concentrated hydrochloric acid and half a gram of metallic tin, granulated or in the form of foil. Upon warming for some time a brown color or precipitate of arsenic is produced (Bettendorf's test).

112. Nascent hydrogen converts arsenic compounds into gaseous hydrogen arsenic, or arsine, AsH_3 . This can be decomposed either by heating or by cooling the flame of the burning gas, the arsenic being deposited as a dark mirror-like coating on cold objects. This is the basis of Marsh's test. For making this many forms of apparatus have been proposed. The simplest of these consist of a small flask (200–300 c.c.) fitted with a doubly perforated stopper, one of rubber being preferable to cork. Through one hole a funnel-tube (a funnel with a piece of rubber tubing slipped over the stem answers for this) passes nearly to the bottom of the flask. The other is provided with an exit tube of difficultly fusible

glass which does not project into the flask and of which the outer end is drawn out to a small point. Into this apparatus is put 5-10 grams of pure granulated zinc, the stopper is inserted and dilute sulphuric (one to four), is poured in through the funnel tube. The hydrogen is allowed to escape until it is judged that all the air has been expelled before the gas is ignited. If there is any doubt of this a towel should first be loosely wrapped about the flask to avoid any flying fragments of glass if there is an explosion. Notice the color of the hydrogen flame, then hold in it a cold porcelain dish, moving it about so as to prevent its becoming excessively heated. If the zinc and acid are both free from arsenic there will be no discoloration of the porcelain. Now pour into the hydrogen flask a few drops of the solution to be tested for arsenic, avoiding as far as possible the introduction of air with it. The color of the flame soon changes to a bluish-white and upon the dish there will be deposited a brownish or black mirror of arsenic. The gas should not be allowed to escape into the room unburned after the arsenic compound is present since the hydrogen arsenid is extremely poisonous. Apply the following tests to the arsenic mirror.

(a) Drop upon it a little of a solution of chlorinated lime (calcium hypochlorite). The mirror dissolves.

(b) Add a drop of concentrated nitric acid. This also dissolves the arsenic. Carefully evaporate this solution to dryness, without heating to a high temperature. Moisten it with a drop of silver nitrate. A brick-red color will be produced if all acid has been removed.

(c) Add to the mirror a few drops of ammonium sulphid. The arsenic is dissolved and the solution, if evaporated to dryness, leaves a yellow residue of arsenic sulphid.

Where the test is to be made more carefully for minute amounts of arsenic, a somewhat larger generating flask is used (perhaps one liter) with more of the zinc. The funnel

tube should be provided with a stop-cock to prevent the admission of air. The gas will contain moisture from the dilute acid, and to remove this should be passed first through an empty U-tube cooled by suspension in water, then through a tube which is filled with lumps of dried calcium chlorid. The latter absorbs the moisture which is not condensed in the first tube. The dry gas now passes through a horizontal tube of glass which does not soften except at a very high temperature ("hard" or "combustion" glass). This tube is to be heated

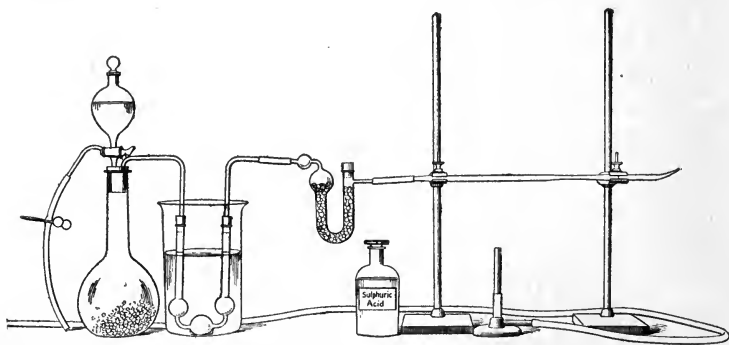


FIG. 12.—Apparatus for the detection of a minute amount of arsenic by Marsh's test.

to redness with a Bunsen burner *after all air has been driven out of the apparatus*. Before introducing the arsenic solution, while the hydrogen is passing through it, the tube should be heated for half an hour to prove the purity of the reagents used. The presence of arsenic is denoted by a brown or black mirror in the part of the tube immediately beyond the flame. If the glass is at this place contracted to a small diameter the mirror is more evident. If any of the arsenic compound is not decomposed here, which is usually the case, it can be tested for in the flame at the pointed end of the tube by means of the cold porcelain, as described above. During the test the escaping gas should be burned at the end of the tube

passed into a solution of silver nitrate to prevent the hydrogen arsenid from escaping into the air. With silver nitrate it forms a precipitate of metallic silver (black) and the arsenic dissolves in the liquid. In long operations it is advisable to provide a means of removing the exhausted acid without the admission of air. This may be affected by inserting through a third hole in the stopper a bent glass tube closed at the outer end by a clamped rubber tube. By opening the clamp and closing the exit tube for a second the liquid can be siphoned from the flask. Where very minute amounts of arsenic are sought the operation may last for several hours.

The arsenic mirror in the tube, when gently warmed in a slow stream of dry hydrogen sulphid, is converted into yellow arsenous sulphid. The reactions made with the mirror on porcelain can be applied here also.

By Marsh's test less than one one-hundredth of a milligram of arsenic in a cubic centimeter has been detected. It is interfered with or prevented by the presence of oxidizing agents, organic matter, and the salts of some heavy metals like mercury.

113. Freshly precipitated ferric hydroxid (54) removes arsenous acid or arsenites from their solutions, as can be seen by shaking an excess with the arsenical liquid, filtering and testing the filtrate for the arsenic. Magnesium hydroxid or oxid acts in a similar manner.

114. The hydroxid ion and the carbonate ion precipitate neither arsenous nor arsenic ions.

Antimony, Sb

The metal is of a white color with a bright luster and is very brittle. It does not dissolve in hydrochloric acid, but is converted to a chlorid by aqua regia. Concentrated nitric acid changes it into a white metantimonic acid that is nearly insol-

uble in the nitric acid. Its soluble compounds, in large doses, are poisonous.

For the reactions a 1-per-cent. solution of $\text{KSbOC}_4\text{H}_4\text{O}_6$ may be used.

115. The sulphid ion precipitates from acid solutions orange-red antimonous sulphid, Sb_2S_3 . It is soluble in ammonium sulphid, as well as in the other alkaline sulphids, to the sulphantimonate which, like the corresponding arsenic compound, is decomposed by acids with the precipitation of Sb_2S_5 . It is insoluble in ammonium carbonate. Boiling concentrated hydrochloric acid dissolves it, but it is insoluble in dilute acids.

116. Metallic zinc precipitates from solutions which contain no nitric acid fine, black, metallic antimony. If, in an antimony solution containing an excess of hydrochloric acid, a piece of platinum foil is brought in contact with the zinc, the antimony is deposited as a dark-brown or black stain on the platinum. This can be removed by hot nitric acid, but does not dissolve in hydrochloric acid.

117. With nascent hydrogen, in a Marsh's apparatus (112), the antimony is converted into hydrogen antimonid, SbH_3 , a gas which is decomposed like the AsH_3 with the formation of an antimony mirror. It has these points of difference:

(a) It is usually of a more sooty black, although this may not be evident where only a very small amount is present.

(b) In the tube of the Marsh's apparatus it is formed on both sides of the spot where the glass is heated, and is not so easily volatile as the arsenic.

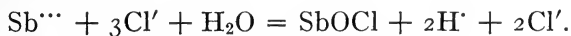
(c) It does not dissolve in a solution of calcium hypochlorite.

(d) It dissolves in a drop of concentrated nitric acid, but upon subsequent evaporation to dryness and moistening with silver nitrate solution it remains colorless.

(e) When warmed in a current of dry hydrogen sulphid gas it is changed into red or black antimonous sulphid.

(f) In ammonium sulphid it dissolves and upon evaporation to dryness the orange red sulphid, Sb_2S_3 , remains.

118. Many of the soluble antimony salts are hydrolyzed by large quantities of water with the precipitation of basic salts. This is true of the chlorid which is changed into the basic chlorid. It sometimes occurs also when antimony solutions are slightly acidified by hydrochloric acid. The precipitate dissolves in a larger amount of the acid or in tartaric acid and is prevented from appearing if the tartaric acid is added previously.



119. With Reinsch's test (108) antimony compounds give a dark coating on the copper, but by heating in the open tube this forms amorphous Sb_2O_3 which can be distinguished from the arsenic compound by the aid of the microscope (94).

120. Gutzeit's test (109) gives immediately a black or brown stain of silver antimonid, Ag_3Sb , on the paper, not a yellow one.

121. Fleitmann's test (110) gives no result with antimony compounds.

122. Tannic acid with the antimony ion forms a white precipitate of antimony tannate, soluble in tartaric acid.

123. With Bettendorf's test (111) the antimony compounds are decomposed, antimony being deposited as a black coating on the tin.

124. The hydroxid ion or the carbonate ion precipitates white antimonous hydroxid $\text{Sb}(\text{OH})_3$.

Tin, Sn

The metal dissolves in concentrated hydrochloric acid, forming stannous chlorid. Concentrated nitric acid changes it into a white metastannic acid insoluble in excess. In concentrated aqua regia tin dissolves to stannic chlorid.

There are two series of tin compounds, the stannous and

the stannic. The former are readily converted into the latter by oxidizing agents or by standing exposed to the air.

The Stannous Ion (Sn^{++})

Use a 2-per-cent. solution of SnCl_2 for the reactions.

125. The sulphid ion in neutral or acid solutions precipitates stannous sulphid, SnS , a dark brown compound. It dissolves in boiling hydrochloric acid. It is insoluble in colorless ammonium sulphid, but soluble in the yellow ammonium sulphid to a sulpho-stannate, $(\text{NH}_4)_2\text{SnS}_3$. From this solution acids precipitate yellow stannic sulphid, SnS_2 , mixed with sulphur.

126. The hydroxid ion precipitates white stannous hydroxid, $\text{Sn}(\text{OH})_2$. It is insoluble in excess of ammonium hydroxid, but is soluble in excess of sodium hydroxid or potassium hydroxid, forming Na_2SnO_2 , from which compound boiling precipitates stannous oxid, SnO .

127. Metallic zinc precipitates dark gray or black, spongy, metallic tin from solutions containing hydrochloric acid. If platinum foil is present it is not discolored.

128. The mercuric ion in hydrochloric acid solution is reduced to the mercurous ion and (compare 87) gives a white precipitate of mercurous chlorid, HgCl , which turns black upon being made alkaline with ammonium hydroxid.

The Stannic Ion (Sn^{+++})

Use for reactions a 2-per-cent. solution of SnCl_4 .

129. The sulphid ion in excess precipitates from acid or neutral solutions yellow stannic sulphid, SnS_2 . It dissolves in boiling hydrochloric acid and in the alkaline sulphids to a sulpho-salt (125) and is reprecipitated unchanged by acids.

130. Zinc gives the same result as with the stannous ion.

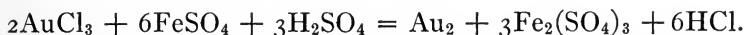
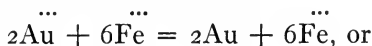
Gold, Au

Gold is insoluble in nitric, hydrochloric, or sulphuric acids. It dissolves in aqua regia or in other liquids where chlorine is set free, forming the chlorid AuCl_3 , and also is soluble in potassium cyanid.

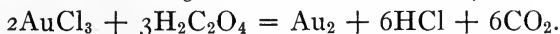
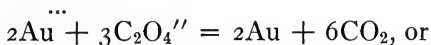
A very dilute solution of the chlorid may be used for the reactions.

131. The sulphid ion precipitates solutions of gold as a dark brown auric sulphid, Au_2S_3 , that is soluble in alkaline polysulphids and in aqua regia, but not in single acids.

132. The ferrous ion precipitates from acid solutions metallic gold as a yellowish-brown powder.



133. Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, also precipitates the metallic gold from its solutions.



The last two reagents precipitate the gold because of their power of reduction. Other reducing agents act in a similar manner.

134. Stannous chlorid containing a little stannic chlorid, SnCl_4 , formed by partly oxidizing the stannous solution, forms with gold solutions a purple compound of varying composition, called the Purple of Cassius. It remains in suspension giving a purple color to the liquid.

135. Metallic zinc, iron, copper or mercury, as well as some other metals, will precipitate the gold in the dark, finely divided metallic form.

136. Ammonium hydroxid, in concentrated gold solutions, forms a precipitate of reddish-brown fulminating gold which, when dry, explodes violently by friction.

137. Compounds of gold are decomposed, the metal being precipitated, by organic matter, *e.g.*, by boiling with sugar.

138. Very minute quantities of gold can be detected by extracting the metal from the finely powdered material by means of tincture of iodine. It should be left in contact for some time to insure an effective solution. If, then, a piece of absorbent white paper is dipped in the solution and afterward dried and burned the gold will color the ash purple. The test is more delicate if the paper is dipped and dried several times before ignition.

Platinum, Pt

The metal is not soluble in single acids, but it dissolves in aqua regia, although not so readily as does gold. This solution contains hydrochlorplatinic acid, H_2PtCl_6 .

A 1-per-cent. solution of H_2PtCl_6 may be used for the reactions.

139. The sulphid ion in acid solutions precipitates slowly (best with the aid of heat) platinic sulphid, PtS_2 . This is a nearly black compound, insoluble in single acids, but soluble in alkaline polysulphids. From this, acids reprecipitate the sulphid. It is also soluble in aqua regia.

140. The ammonium or potassium ion precipitates from hydrochloric acid solutions a double salt—ammonium chlorplatinite, $(\text{NH}_4)_2\text{PtCl}_6$, or potassium chlorplatinite, K_2PtCl_6 . These are yellow crystalline salts, somewhat soluble in water and rendered less so when alcohol is present.

141. Metallic zinc or iron precipitates the platinum as spongy black metallic platinum.

142. Oxalic acid does not precipitate platinum solutions and the ferrous ion does so only after long boiling. Some organic substance, however, like sugar or alcohol, will decompose boiling alkaline solutions, the metal being thrown down as a fine black powder—platinum black.

Directions for the Separation of the Cations of Group II

If the solution does not contain free acid, make it acid by the addition of hydrochloric. Precipitate all the ions of the group with hydrogen sulphid. This may be done by allowing the gas to pass through the solution, or by the use of a solution of hydrogen sulphid in water until a precipitate no longer appears. Warm and stir the liquid until the precipitate settles, then when the metals have been completely precipitated filter and wash. Groups III, IV, and V pass into the filtrate. Group II is divided into two divisions, A and B, according to whether it is insoluble (A) or soluble (B) in yellow ammonium sulphid. Scrape the precipitate from the filter or rinse it off with the aid of 15 c.c. of yellow ammonium sulphid into a small porcelain dish.¹ Heat gently, but not to boiling and keep it at this temperature for five minutes, stirring often. Filter and wash, discarding the wash water. If the precipitate has a tendency to pass through the filter this may be prevented by warming with 5 c.c. of ammonium chlorid solution.

Division A—Sulphids Insoluble in Yellow Ammonium Sulphid

The precipitate, obtained by saturating the acidified solution with hydrogen sulphid, contains the sulphids of mercury, lead, bismuth, copper, and cadmium.

After the precipitate has been well washed rinse it from the paper with 10 c.c. of dilute nitric acid and boil. The sulphids are all dissolved with the exception of the black mercuric sulphid which remains as a heavy sediment. A part of the lead sulphid may be oxidized to lead sulphate, an insoluble, white,

¹ Instead of at first treating the whole precipitate with ammonium sulphid, it is better to test a small portion thus to learn if B is present. If it is, treat the whole in the same manner; if not, proceed directly to the examination for A. If it dissolves completely A is absent.

heavy powder. Sulphur may also be present as a grayish, floating powder. Filter out the precipitate, wash it and, after removing from the paper, dissolve it. Filter off the sulphur and test the filtrate with a few drops of stannous chlorid. The mercury is precipitated as a white chlorid which becomes gray with an excess of the tin solution or after heating.

The solution of lead, bismuth, copper, and cadmium should be evaporated nearly to dryness under a hood, then diluted to 10 c.c. with water and tested for lead by adding dilute sulphuric acid (avoiding a large excess) and half a dozen drops of alcohol. Lead sulphate, a fine, white, heavy powder is thrown down. It should be allowed to settle before filtering and, if necessary, a little more alcohol added to insure a complete precipitation. Filter and wash. The lead may be confirmed by pouring 3-4 c.c. of sodium hydroxid upon the washed lead sulphate without removing from the filter, then adding ammonium sulphid to the filtrate when the black lead sulphid should be formed.

To the filtrate from the precipitated lead sulphate, which contains bismuth, copper, and cadmium, add ammonium hydroxid until it smells strongly of this reagent. The bismuth is precipitated as a white flocculent hydroxid while the copper and cadmium dissolve in excess, the former giving a deep blue solution. Filter, wash, and confirm the bismuth by the addition of a few drops of sodium hydroxid and as much stannous chlorid, to the substance on the paper, when the compound turns black.

If a blue color indicates copper in the filtrate from the bismuth, acidify one-half and confirm the copper by potassium ferrocyanid which produces a reddish-brown precipitate. To the remainder add potassium cyanid until the blue color disappears, then precipitate the bright yellow cadmium sulphid by hydrogen sulphid. If no blue color is present the

copper is probably absent, in which case the potassium cyanid may be omitted and the whole filtrate from the bismuth may be tested for cadmium.

Division B—Sulphids Soluble in Yellow Ammonium Sulphid

This contains the sulphids of arsenic, antimony, tin, gold, and platinum. Acidify the filtrate with hydrochloric acid. The sulphids of metals are precipitated in curdy masses. If the precipitate is fine and nearly white and settles very slowly it is only sulphur and may be neglected. Otherwise filter and wash, adding ammonium chlorid as above if the filtrate is not clear.¹ From the precipitate which contains the sulphids of all the metals of Division B, dissolve the arsenic sulphid by digesting several minutes with about 10 c.c. of ammonium carbonate, then filter. The arsenic can be detected in the filtrate by acidifying with hydrochloric acid, then passing in hydrogen sulphid; yellow arsenious sulphid is precipitated.

The well-washed precipitate should have the water removed from it as far as possible by draining and pressing, then after removal from the paper is to be warmed in about 5 c.c. of concentrated hydrochloric acid for several minutes. This should be done under a hood and the acid must not be allowed to boil violently. The sulphids of antimony and tin dissolve, and those of gold and platinum remain, mixed with some sulphur and possibly a part of the arsenic sulphid.

After filtering pour the filtrate into a dish, add a few fragments of zinc and immediately bring a piece of platinum foil into contact with this. If antimony is present it will make a brown or black stain on the foil to which it adheres very firmly. The tin is precipitated in the metallic form, but nearly black in color and so heavy that it quickly settles to

¹ As the filtrate is not to be used it may, for economy of time, be decanted without filtration.

the bottom. Let the action proceed until it seems certain that all the antimony and tin are precipitated, then wash the tin by decantation and dissolve it in one or two cubic centimeters of warm concentrated hydrochloric acid. This solution when added to mercuric chlorid precipitates white mercurous chlorid, which turns black if the liquid is made alkaline with ammonia. If the stannous chlorid is in excess it sets free gray metallic mercury from the mercurous chlorid.

The antimony can be confirmed, if thought desirable, by warming the coated foil in 2-3 c.c. of yellow ammonium sulphid in a test-tube, then evaporating to dryness. Orange-red antimonous sulphid remains.

The remaining precipitate from which the sulphids of arsenic, antimony, and tin have been dissolved by ammonium carbonate and hydrochloric acid will be dark colored if it contains the sulphid of gold or platinum. Otherwise it will consist of sulphur with possibly some arsenic sulphid that the ammonium carbonate did not completely dissolve. If it is dark in color, warm it with aqua regia to dissolve the gold and platinum, filtering if solution is not complete. Test half the filtrate for gold with a mixture of stannous and stannic chlorids (Purple of Cassius, 134). From the other half, precipitate the yellow, crystalline ammonium chlorplatinate with NH_4Cl , using a rather concentrated solution. Confirm this by examination with the microscope (140).

TABLE IV

OUTLINE OF THE SEPARATION OF THE CATIONS OF GROUP II

From the acidified solution precipitate with H_2S . The precipitate contains all the metals as sulphids. Filter and wash. Warm the precipitate in yellow ammonium sulphid. Filter and wash. The filtrate contains the sulphids of As, Sb, Sn, Au, and Pt (Division B). The precipitate contains HgS , PbS , Bi_2S_3 , CuS , and CdS (Division A).

DIVISION A

After the precipitate, formed by H_2S , has been washed, boil it with HNO_3 and filter.

A black insoluble residue is HgS , often mixed with sulphur and PbSO_4 . Warm it with aqua regia, and after filtering add SnCl_2 . White HgCl is precipitated, changed to gray Hg with excess of the reagent.	The solution contains Pb , Bi , Cu , and Cd . Evaporate it nearly to dryness under a hood. Dilute with water and precipitate the Pb with dilute H_2SO_4 and a few drops of alcohol, if necessary for complete precipitation. Filter and wash.		
	The precipitate is PbSO_4 . Dissolve in NaOH and add to the solution H_2S . Black PbS is produced.	The filtrate contains Bi , Cu , and Cd . Add NH_4OH in excess and, if there is a precipitate, filter.	
		$\text{Bi}(\text{OH})_3$ is the precipitate. After it has been washed moisten it on the paper with NaOH then with SnCl_2 . It turns brown or black.	The presence of Cu in the solution is indicated by the blue color. Acidify one part and add $\text{K}_4\text{Fe}(\text{CN})_6$. $\text{Cu}_2\text{Fe}(\text{CN})_6$, a reddish-brown compound appears.
			To the other part add KCN until it is colorless, then H_2S . Yellow CdS is precipitated. In absence of Cu omit KCN .

DIVISION B

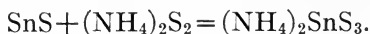
Acidify the filtrate slightly with HCl . The As_2S_3 , Sb_2S_3 , SnS_2 , Au_2S_3 , and PtS_2 are precipitated with fine white sulphur. Filter and wash, discarding the filtrate. Warm the mixed sulphids for several minutes in a test-tube with $(\text{NH}_4)_2\text{CO}_3$. Filter and wash.

<p>The solution contains the As. Acidify with HCl, add H₂S; yellow As₂S₃ precipitates.</p>	<p>The insoluble residue contains Sb₂S₃, SnS₂, Au₂S₃, and PtS₂. As far as possible remove water, place in a porcelain dish and warm under a hood with concentrated HCl. Filter.</p>		
	<p>The filtrate contains Sb and Sn. Add a little Zn, and touch it with a Pt foil. The Sb makes a brown deposit on the Pt. The Sn is precipitated as a heavy black powder. Wash this by decantation and dissolve in concentrated HCl. A few drops of HgCl₂ gives a white precipitate, HgCl (blackened by NH₄OH), or gray Hg.</p>	<p>The insoluble residue contains only S and (possibly) As₂S₃ if it is light-colored. If Au₂S₃ or PtS₂ is present it is dark-colored. In the latter case warm it with aqua regia and filter out any insoluble residue. The filtrate contains Au and Pt. Divide it into two portions. To one add stannous and stannic chlorides. A purple color indicates gold. To the other add NH₄Cl. Yellow precipitate of (NH₄)₂PtCl₆.</p>	
	<p>If the foil is rinsed, then warmed in (NH₄)₂S_x, the Sb is dissolved and after evaporation to dryness leaves orange-red Sb₂S₃.</p>		

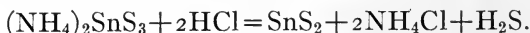
Explanation of the Separation of the Cations of Group II

If group I has previously been removed from the solution it will contain hydrochloric acid, otherwise this must be added, partly to favor the precipitation of some of the sulphids in this group, partly to prevent a precipitation of some of those of group III. A large amount of hydrogen sulphid will be necessary because the solution cannot be made concentrated and the gas precipitates slowly.

Arsenic, antimony, and tin sulphids are all converted into soluble sulpho-salts by the ammonium sulphid. In the case of stannous sulphid the yellow or polysulphid is necessary. This is made by dissolving sulphur in the colorless sulphid, when one or more atoms of sulphur are added to the molecule, forming $(\text{NH}_4)_2\text{S}_x$ where x = two or more. The tin is changed to a stannic compound when it dissolves.

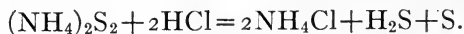


Acidifying decomposes the sulpho-salt and precipitates the tin as a stannic, not a stannous, sulphid.



In the digestion of the mixed groups with yellow ammonium sulphid boiling must be prevented because this would decompose the ammonium sulphid.

Sulphur is always precipitated, white because of its fineness, when a polysulphid is acidified.



Explanation of the Separation of the Cations of Group II, Division A

The sulphids of copper, bismuth, and cadmium dissolve in boiling nitric acid, forming nitrates, and lead¹ does so for

¹ Although lead is classified with the metals of group I, it will, if present, be found in part in group II.

the most part, but may be partly oxidized to insoluble lead sulphate. This remains with the mercuric sulphid which does not dissolve in a single acid. The lead compound does not become soluble by the action of aqua regia but the mercuric sulphid is changed to the chlorid. The action of the tin chlorid is as described in 87.

The portion of the lead which went into solution with the other metals can be precipitated as the sulphate, but since the presence of much free nitric acid will to some extent prevent this, thus leaving some of the metal to interfere with future tests, it is better to remove the acid. To accomplish this the evaporation must be carried so far that but a very small bulk remains as the acid is driven off only after the water, in the last stages of the operation. The lead sulphate is not entirely insoluble, but can be made more so when alcohol is present. The acid should be added as long as a precipitate appears, but a great excess is objectionable because of the large amount of ammonium hydroxid which it would necessitate in the next step.

A very small quantity of copper gives the blue color with ammonium hydroxid, which must be in excess to produce it. If the color is well-marked the ferrocyanid test may be unnecessary.

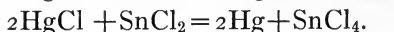
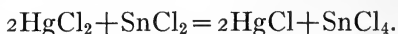
It is necessary to confirm the bismuth by some other test than precipitation by ammonium hydroxid as if any of the lead had remained unprecipitated by sulphuric acid it also would form a white precipitate here. It does not, however, respond to the confirmatory test for bismuth.

The addition of potassium cyanid before testing for cadmium is to prevent the precipitation of the copper as a sulphid by hydrogen sulphid (69, 82). This being so much darker than the cadmium sulphid, the latter would probably escape detection.

Explanation of the Separation of the Cations of Group II, Division B

Of the precipitated sulphids only that of arsenic is soluble in ammonium carbonate, from which solution it is precipitated as As_2S_3 by acidifying. Either Gutzeit's or Reinsch's test will react with the suspended arsenous sulphid without its being filtered from the liquid.

The stannic sulphid with hydrochloric acid dissolves to SnCl_4 , and the antimony sulphid to SbCl_3 . The antimony compound is with difficulty attacked by the acid and for this reason it must be as far as possible free from water to avoid dilution of the acid. Boiling would drive off the gaseous HCl . The chlorids of tin and antimony are both reduced to the metal by nascent hydrogen. This is produced by the action of an acid on zinc. If platinum is present the antimony is deposited upon it, but the tin is not. Zinc almost always contains impurities which remain after it has dissolved. They are often black in color, but float in the liquid while the tin is heavy and quickly settles. To confirm it the stannous chlorid is produced by the aid of concentrated hydrochloric acid and this is added to 2-3 c.c. of mercuric chlorid, yielding white mercurous chlorid or gray metallic mercury. The reactions are as follows:



The fine coating of metallic antimony dissolves readily in yellow ammonium sulphid to the sulphantimonite and this is decomposed by the heat of evaporation to antimonous sulphid.

The sulphids of gold and platinum which do not dissolve in a single acid do so in aqua regia and can be precipitated from this by the ordinary reagents.

Practical Exercises in Group II

1. Mix in a beaker 3-5 c.c. each of solutions of mercury, lead, copper, bismuth, and cadmium, and, after precipitating with hydrogen sulphid, separate the metals according to Table IV, division A.

2. In the same manner precipitate a mixture of the solutions of arsenic, antimony, and tin with hydrogen sulphid and separate the mixed sulphids according to Table IV, division B.

3. For practice in separation of the group into its two divisions mix in the same way one or two from each division, *e.g.*, mercury, copper, arsenic, and antimony. In making the selection it should be remembered that stannous chlorid reduces mercuric compounds and that this and other chlorids precipitate lead in part, also that to keep bismuth, and sometimes antimony, in solution after dilution a considerable quantity of acid is required.

4. For further practice make analyses of unknown mixtures of the metals of group II furnished by the instructors.

Questions for Further Study on Group II

What use is made in medicine of the fact that arsenous acid forms an insoluble compound with ferric or magnesium hydroxid? How should the ferric hydroxid be prepared for this purpose and what will be the most convenient materials? Soluble salts of what metals would be incompatible with solutions of arsenites and arsenates? Is the insolubility of the arsenites and arsenates of the heavy metals sufficient to render these compounds non-poisonous? What classes of soluble compounds would be incompatible with solutions of metals of group II? Where and how is cupric hydroxid used in testing for glucose? What is the difference between the red and

the black mercuric sulphid? between yellow and red mercuric oxid? What is the pharmaceutical name of the yellow oxid and how is it prepared? What pharmaceutical names are applied to the mercuric aminochlorid? What medicinal substances have sufficient reducing powers to take the whole or a part of the chlorin from mercuric chlorid? With what class of medicinal compounds would a solution of mercuric chlorid in an excess of potassium iodid be incompatible? What compound of antimony most commonly causes acute poisoning? Could any of the above reagents be safely used to render it insoluble in the gastric juice? If so in what form or preparations could it be most conveniently obtained?

GROUP I

Lead, Silver, and Mercury (Mercurous Compounds)

They are precipitated from their solutions by the chlorid ion. Their sulphids, carbonates, phosphates, oxids, hydroxids, arsenates, arsenites, bromids, and iodids, as well as their chlorids, are insoluble in water, although lead chlorid is somewhat soluble.

Lead, Pb

Lead is soluble in dilute nitric acid, more easily by the aid of heat, but is little affected by hydrochloric or sulphuric acids. Its soluble compounds are poisonous.

A great number of organic substances form insoluble compounds with lead acetate, which can consequently be used to remove them from solution.

For the reactions use a 5-per-cent. solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

143. The sulphid ion gives with lead solutions a black precipitate of lead sulphid, PbS , soluble in dilute nitric acid, sulphur being set free at the same time. If very concentrated nitric acid is used sulphuric acid is formed from the sulphur and this converts the lead into insoluble, white, lead sulphate, PbSO_4 .

144. The hydroxid ion precipitates lead hydroxid, $\text{Pb}(\text{OH})_2$. This dissolves in an excess of sodium hydroxid or potassium hydroxid with the formation of a plumbate of the alkali metal, Na_2PbO_2 or K_2PbO_2 . It does not dissolve in an excess of ammonium hydroxid.

145. The carbonate ion precipitates white lead carbonate. Since the soluble carbonates easily hydrolyze, the reagent usually contains OH' , and, consequently, the hydroxid precipitates with the carbonate, perhaps as $(\text{PbCO}_3)_2\text{Pb}(\text{OH})_2$. It is soluble in acids, except sulphuric.

146. The chlorid ion in concentrated solutions of lead salts forms a heavy white precipitate of lead chlorid, PbCl_2 . This dissolves in hot water and on cooling, separates again in the form of needle-shaped crystals.

147. The sulphate ion gives a fine, heavy, white precipitate of lead sulphate, PbSO_4 . From very dilute solutions it only appears after standing a long time. Free acids, except sulphuric, hinder its separation and alcohol hastens it. Lead sulphate dissolves in sodium hydroxid.

148. The chromate or dichromate ion precipitates yellow lead chromate, PbCrO_4 , soluble in nitric acid or sodium hydroxid.

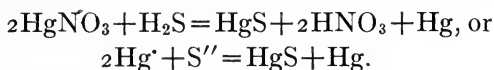
149. The iodid ion precipitates yellow lead iodid, PbI_2 , from not too dilute solutions. This dissolves in boiling water from which it separates as the water cools.

150. Tannic acid precipitates yellowish lead tannate.

The Mercurous Ion, Hg'

Use for the reactions a 1-per-cent. solution of HgNO_3 .

151. The sulphid ion produces with the mercurous ion a black precipitate of mercuric sulphid mixed with mercury.



152. The hydroxid ion if obtained from compounds of so-

dium, potassium, or calcium forms a black precipitate of mercurous oxid, Hg_2O , insoluble in excess.

153. Ammonium hydroxid precipitates a black mercurous amino salt.



154. The chlorid ion precipitates fine, white, heavy mercurous chlorid, HgCl . This is soluble in aqua regia, being slowly converted into mercuric chlorid, HgCl_2 . It dissolves with much difficulty in nitric or hydrochloric acids singly. Ammonium hydroxid changes it into black mercurous amino-chlorid. Dry HgCl is slowly changed by sugar and some other organic substances into HgCl_2 and Hg .

155. The iodid ion precipitates greenish-yellow mercurous iodid, HgI .

156. Metallic copper and the stannous ion give the same reactions as with the mercuric compounds. Other reducing agents act like the stannous ion.

157. Nitric acid and other oxidizing agents change mercurous to mercuric compounds.

Boil 2-3 c.c. of mercurous nitrate solution for a minute with 1-2 c.c. of concentrated nitric acid. HCl will not produce a precipitate. (Compare 154.)

Silver, Ag

Nitric acid readily dissolves silver, but it does not dissolve in hydrochloric acid. Its soluble salts are poisonous.

Use for the reactions a 1-per-cent. solution of AgNO_3 .

158. The sulphid ion precipitates black silver sulphid, Ag_2S , which dissolves in boiling nitric acid.

159. The chlorid ion gives a precipitate of heavy, curdy, white silver chlorid, AgCl . At the time of precipitation it is white, but by exposure to the light it gradually turns violet, then gray, and finally black. In very dilute solutions it does not precipitate at first, the liquid becoming opalescent or

milky. From this the precipitate slowly settles after it has stood for some time, or more rapidly by boiling. Silver chlorid is not soluble in nitric acid, but dissolves readily in ammonium hydroxid and is reprecipitated from this solution by acidifying with nitric acid.

160. The hydroxid ion precipitates white silver hydroxid which quickly changes to the dark brown silver oxid, Ag_2O . This is insoluble in excess of sodium or potassium hydroxid but with ammonium hydroxid it forms a complex ion, $\text{Ag}(\text{NH}_2)_3^-$, becoming soluble.

161. The chromate or dichromate ion forms a dark red precipitate of silver chromate, Ag_2CrO_4 .

162. Zinc, copper, mercury, tin, or lead precipitate the metal.

163. Ferrous sulphate, FeSO_4 , and other reducing agents convert the silver ion into the metal.

Separation of the Cations of Group I

Add hydrochloric acid to the solution. Silver and mercury (ous) are precipitated with most of the lead as chlorids. Filter and wash in cold water. Make a hole in the apex of the filter and rinse the precipitate with 10–15 c.c. of water into a test-tube. Heat to boiling and filter while hot. The lead chlorid is dissolved. Test a portion of the filtrate after it is cold for this with dilute sulphuric acid. A fine white precipitate of lead sulphate is formed. From another portion with potassium dichromate precipitate yellow lead chromate.

After the precipitated chlorids of silver and mercury have been washed with hot water on the filter, pour over it 10 c.c. of warm ammonium hydroxid, receiving the filtrate in a clean test-tube. The silver chlorid dissolves. Mercurous chlorid is changed to a black solid which remains upon the filter.

Acidify the filtrate with nitric acid. The silver chlorid appears as a white precipitate or opalescence, soluble in ammonia and reprecipitated by nitric acid.

TABLE V

OUTLINE OF SEPARATION OF THE CATIONS OF GROUP I

To the solution of the mixed ions add HCl in excess. Filter and wash in cold water. The precipitate contains PbCl_2 , AgCl , and HgCl . All other groups present in the original solution pass into the filtrate. Boil the precipitate with water, filtering hot.

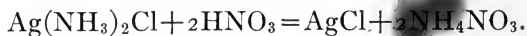
The filtrate contains Pb. Test part with H_2SO_4 ; a fine white precipitate is lead sulphate.	The insoluble residue contains AgCl and HgCl . Dissolve the AgCl in warm NH_4OH .	
Test part with $\text{K}_2\text{Cr}_2\text{O}_7$; a yellow precipitate is lead chromate.	Acidify the filtrate with nitric acid; a white precipitate is AgCl .	The mercury remains as black, insoluble $\text{NH}_2\text{Hg}_2\text{Cl}$.

Explanation of the Separation of the Cations of Group I

This depends upon the solubility of the chlorids, lead chlorid dissolving in hot water but not easily in cold, and silver chlorid in ammonium hydroxid and not in hot water, the mercurous chlorid being insoluble in both.

The lead can be confirmed in the aqueous solution by any of its characteristic precipitants.

With ammonium hydroxid silver chlorid forms ammonio-silver chlorid, $\text{Ag}(\text{NH}_3)_2\text{Cl}$, which is soluble. It is decomposed by acids the silver chlorid separating again.



The identification of the mercurous chlorid is without difficulty since it is the only one of the three which gives a dark color with ammonium hydroxid.

Practical Exercise on Group I

Mix in a test-tube 4-5 c.c. each of solutions of silver, lead, and mercurous ions and make the separation as given above.

Questions for Further Study on Group I

Would the compounds of lead which are formed as precipitates be necessarily insoluble in the gastric juice? Are

there any of the reagents which might be employed in cases of acute lead poisoning as antidotes? Would all of those which form insoluble compounds and which would thus prevent absorption, be suitable for such a purpose? What organic compounds commonly used medicinally would be incompatible with lead compounds? What is the common name of lead carbonate? In accordance with the above reactions what would be a safe and easily obtainable antidote for a poisonous dose of mercurous or silver nitrate? What is the pharmaceutical name of mercurous chlorid? How does it compare in its chemical properties and physiological action with mercuric chlorid? Would the chemical antidotes for the mercurous ion necessarily precipitate mercuric chlorid? What is the danger of leaving dry mercurous chlorid for a long time mixed with organic substances? What is a simple method of testing calomel for small quantities of mercuric chlorid? What is the pharmaceutical name of mercurous oxid and how is it prepared? Where is the turning dark of silver chlorid by light made use of practically?

The Separation of Metals into Groups

The different metals can be precipitated in succession in groups from the original solution by using these group reagents in the following order:

1. Hydrochloric acid, which precipitates group I, silver, the mercurous ion and lead (in part).

2. Hydrogen sulphid, which precipitates group II, lead (remainder), the mercuric ion, copper, bismuth, cadmium, arsenic, antimony, tin, gold, and platinum.

3. Ammonium sulphid (in the absence of phosphates, oxalates, borates, citrates, and tartrates), which precipitates group III, cobalt, nickel, iron, manganese, chromium, zinc, and aluminum.

4. Ammonium carbonate, which precipitates group IV, barium, strontium, and calcium, but not magnesium.

Magnesium, sodium, potassium, and ammonium are not precipitated by any of the above reagents:

[The details of the separation are as follows:

[To the cold solution which may contain all the ions add hydrochloric acid¹ as long as any precipitate forms. This contains group I. Separate the metals according to Table V. Filter, and to the filtrate add hydrogen sulphid until the liquid smells of this gas. Warm, stir to make the precipitate collect in large masses, then, if the precipitation is complete, filter and wash with warm water. The metals of group II are on the filter, the remainder of the groups in the filtrate. Make the separation according to Table IV. If the aqueous solution of hydrogen sulphid has been used to precipitate group II, and the filtrate is therefore of large volume, it may be concentrated to 40–50 c.c. by boiling. It should then be made neutral or faintly alkaline by ammonium hydroxid and, after the addition of ammonium chlorid, be precipitated by a slight excess of ammonium sulphid. Warm nearly to boiling, filter, and wash. The precipitate contains the metals of group III. Separate them as in Table II or III. Boil the filtrate until the ammonium sulphid has been decomposed, as is shown by the disappearance of its odor, filtering out the sulphur if any has been set free. Precipitate group IV with ammonium carbonate, warming nearly to boiling to insure its complete separation. Filter and wash. Analyze the group by the use of Table I. If the filtrate is much diluted, evaporate to 10 or 20 c.c. and apply the flame tests for sodium and potassium. Afterward add to the solution sodium phosphate as a test for magnesium. Test the original substance for ammonium.

¹ In precipitating the different groups, when their presence or absence is uncertain, it is usually better to first test only a small portion of the solution with the group reagent, then, if a precipitate forms, to treat the whole in the same manner.

OUTLINE OF ANALYSIS OF SOLUTION WHICH MAY CONTAIN METALS OF ALL GROUPS (IN ABSENCE OF PHOSPHATES, BORATES, ETC.)

Precipitate = AgCl , HgCl , PbCl_2 Boil with water, filter and wash.	Filtrate = Hg' , Pb , Cu , Bi , Cd , As , Sb , Sn , Au , Pt , Ni , Co , Fe , Mn , Cr , Zn , Al , Ba , Sr , Ca , Mg , K , Na , NH_4 . Add an excess of H_2S , warm, filter and wash.	Precipitate = HgS , PbS , CuS , BiS_3 , CdS , As_2S_3 , Sb_2S_3 , SnS or SnS_2 , AuS_2 , PtS_2 . Digest in $(\text{NH}_4)_2\text{S}$ and filter.	Filtrate ¹ contains Ni , Co , Fe , Mn , Cr , Zn , Al , Ba , Sr , Ca , Mg , K , Na , NH_4 . Add NH_4OH , NH_4Cl , and $(\text{NH}_4)_2\text{S}$. Warm, filter and wash.
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Black residue = $\text{NH}_2\text{Hg}_2\text{Cl}$.	Solution = Ag. Acidity with HNO_3 . White precipitate = AgCl .	Filtrate = PbCl_2 . Confirm Pb by H_2SO_4 or	Precipitate = HgS . Dissolve in aqua regia and confirm by SnCl_2 .	Precipitate = PbSO_4 . Dissolve in NaOH and confirm by H_2S .	Filtrate = As. Try Gutzeit's or Reinsch's test.	Filtrate = Sn, Sb, and Pt. Confirm Sn with HCl and Sb by conversion to Sb_2S_3 with $(\text{NH}_4)_2\text{S}_x$.	-In half confirm Au by tin chlorids.	To half add NH_4Cl . Yellow precipitate = $(\text{NH}_4)_2\text{PtCl}_6$.	Insoluble = NiS, CoS. Test with borax and dissolve in aqua regia and separate with $\text{CH}_3\text{CO}_2\text{H}$. (Page 46).	Dissolve part in HCl and confirm Fe by $\text{K}_4\text{Fe}(\text{CN})_6$.	Mn = green mass. Insoluble.	Filtrate = Cr. Confirm with $\text{CH}_3\text{CO}_2\text{H} + \text{Pb}$. (CH_3CO_2) $_2$.	Precipitate = $\text{Al}(\text{OH})_3$.	Filtrate = Zn. Confirm by $(\text{NH}_4)_2\text{S}$ or $\text{K}_4\text{Fe}(\text{CN})_6$ in acid solution.	Precipitate = BaCrO_4 . Confirm by flame.	Filtrate = Sr, Ca. Add H_2SO_4 and filter.	Precipitate = SrSO_4 . Confirm by flame.	Filtrate = Ca. Add NH_4OH and $(\text{NH}_4)_2\text{CO}_3$. Precipitate = CaCO_3 . Confirm by flame.	Test by flame with and without Co glass for K and Na.	Precipitate Mg with $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$.	Test for NH_4 in original solution by NaOH .
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(93)

The Method of Analysis of Alloys Containing

Hg, Ag, Cu, Bi, Pb, Cd, Au, Pt, Sb, Sn, Ni, Co, Fe,
Mn, Cr, Al, Zn

Warm the fine alloy with equal parts of concentrated nitric acid and water under a hood until no gritty particles remain. Au, Pt, Sb and Sn are not dissolved; the others go into solution. Filter and wash.

Evaporate the filtrate nearly to dryness if much acid has been used, dilute, heat to boiling and precipitate Ag while hot, by HCl, filter and precipitate by an excess of H_2S , which forms insoluble sulphids of Hg, Cu, Bi, Pb and Cd. Stir until it settles, then filter and separate metals in the filtrate by Table II. Wash the precipitate well, then rinse it from the paper with about 10 c.c. of nitric acid and separate the metals by Table IV, Division A.

If Au or Pt are contained in the first insoluble residue it will be dark in color. The compounds of Sb and Sn are white. Dissolve the moist precipitate in a little warm aqua regia and, after filtering, boil the solution a minute under the hood to expel the chlorine. Test half for Sn and Sb by metallic zinc and platinum (116, 127) (Table IV, Division B). Evaporate the excess of acid from the other half of the solution under a hood and dissolve in 3-4 c.c. of water. Test a part for Au by SnCl_2 and SnCl_4 , which gives a purple color (purple of Cassius). To the rest add concentrated ammonium chlorid. Pt gives a yellow crystalline precipitate (140).

Practical Exercises on General Analysis

For further drill the student should make analyses of as many unknown substances as possible, where all the groups must be sought for.

Questions for Further Study on the Metallic Compounds

Which of the metals are incompatible with the alkaline hydroxids because of their being precipitated? Does calcium hydroxid have a similar action to that of the hydroxids of the alkali metals? What hydroxids have an alkaline reaction? What carbonates? What ones of the common pharmaceutical preparations have an alkaline reaction? Which groups of metals are precipitated by soluble carbonates? Of which ones are the carbonates soluble in water? What medicinal substances with an oxidizing action are the most commonly used in solution? What ones have a reducing action? What compounds of the metals studied would be so far affected by the last-mentioned reagents as to cause an incompatibility? What classes of compounds would be incompatible with the metallic compounds of group I by rendering them insoluble? with group II? with group III? with group IV? with group V? What pharmaceutical preparations contain tannic acid? Does albumin form insoluble combinations with any other metallic compounds except mercuric salts? Are any compounds decomposed by exposure to light except silver chlorid? What is the usual composition of precipitates produced by the action of a soluble hydroxid on the ion of a soluble metallic salt? by a soluble carbonate? What are the exceptions to the usual rule? Knowing the composition of the reagent used, sulphid, phosphate, chromate, sulphate, etc., can we predict what will be the composition of the precipitate which will be formed with the different cations?

CHAPTER II

ACIDS (ANIONS)

IN testing for the presence of an acid we must distinguish between the acid in the free state and that which is combined as a salt (the hydrogen being wholly or in part replaced by a metal), as the reactions of one form often differ from those of the other. In the second case the reactions are due to the anion; in the first there are, in addition, those of hydrogen ion. Free acids usually turn blue litmus red, but the same is true of many acid salts as well as of some normal salts of the heavy metals (pp. 20, 21). The acids may be classified in a number of groups according to the similarity of their chemical action, but the actual separation of the anions from a complex mixture is not so simple a proceeding as that with the cations.

Sulphuric Acid, H_2SO_4 , and Sulphates (the Sulphate Ion)

164. Pure sulphuric acid is a heavy, oily liquid (sp. gr. 1.85) which generates a large amount of heat when diluted with water, with which it forms a number of compounds. It dissolves many metals as sulphates.

The free acid chars most organic compounds when it is warmed with them by abstracting the elements of water and leaving the carbon. If the acid is dilute, the charring only occurs after the water has been evaporated, leaving the concentrated acid. This can be shown upon paper or wood. Some organic compounds, including oxalic acid and its salts, also some of the alkaloids, are not thus blackened.

For the reactions of the anion a 1-per cent. solution of any sulphate may be used.

165. The barium ion gives, in solutions of the free acid or its salts, a white, heavy, finely divided precipitate of barium sulphate, BaSO_4 , which is insoluble in water, acids, and alkalies.

166. The lead ion precipitates the sulphate ion as heavy, white, finely divided lead sulphate, PbSO_4 . It is somewhat soluble in acids and, after washing, blackens when brought in contact with ammonium sulphid. It is not so sensitive a test as the preceding.

Sulphurous Acid, H_2SO_3 , and Sulphites (the Sulphite Ion)

Sulphurous acid is produced when sulphurous oxid is dissolved in water. It is a colorless liquid with the odor of burning sulphur. It has an acid reaction and bleaches unstable coloring matters like those of the flowers. By exposure to the air it is oxidized readily to sulphuric acid. Its salts undergo the same chemical change. Both are consequently used as reducing agents. Only the sulphites of the alkalies are soluble in water.

For the reactions use sodium sulphite.

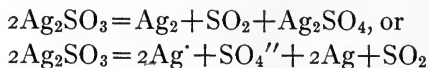
167. Sulphites are decomposed by sulphuric acid with the evolution of SO_2 , a heavy colorless gas which smells like burning sulphur. If a large test-tube is allowed to fill with it, after adding a little acid to a crystal of the sulphite, and the gas is then poured into another tube containing dilute potassium permanganate solution, the latter is decolorized.

Oxidizing agents like nitric acid, bromin or chlorin water, and many others convert sulphites into sulphates, which then give with the barium ion a precipitate that is insoluble in acids.

168. The barium ion gives with a neutral solution of a sulphite a white precipitate of barium sulphite, BaSO_3 , which dissolves in hydrochloric or nitric acids.

169. The silver ion precipitates the sulphite ion as white silver sulphite, Ag_2SO_3 , which upon warming turns black with

a formation of metallic silver and sulphur dioxide and silver sulphate.



170. The sulphite ion evolves hydrogen sulphid when warmed with dilute sulphuric acid and zinc. This gas turns lead acetate paper brown or black, and can be identified by its odor likewise.

Carbonic Acid, H_2CO_3 , and Carbonates (the Carbonate Ion)

Carbon dioxide (carbon anhydride) when dissolved in water forms carbonic acid, H_2CO_3 , which reddens litmus-paper. The acid exists only in salts and in solution, which latter is readily decomposed by heating, the carbon dioxide being expelled. Of the carbonates only those of the alkalis are very soluble in water and these when dissolved have in consequence of hydrolysis a strong alkaline reaction.

For the reactions sodium carbonate may be used.

171. Carbonates are decomposed by almost all free acids, usually without heating, although this is sometimes necessary. The gas which escapes with effervescence is carbon dioxide. It can be identified by its rendering lime-water milky. It is a colorless, odorless gas, so much heavier than air that it can be poured from the test-tube where it is evolved into another containing 2 or 3 c.c. of lime-water. If the tube is now shaken so as to mix the two, the liquid is turned white—a characteristic reaction. It may also be shown by holding a drop of the lime-water down in the tube of the gas on the end of a glass rod, being careful not to let the drop run off by touching the side of the tube. The precipitate dissolves in HCl .

172. The acid carbonates or bicarbonates, like NaHCO_3 , are less stable than the normal carbonates, like Na_2CO_3 or

CaCO_3 , and are decomposed when heated in water before this reaches its boiling-point, half the carbon dioxid escaping. The normal carbonates are not thus decomposed. Soluble normal carbonates will also turn yellow turmeric paper reddish-brown, while the acid carbonates do not if they contain none of the normal compound, although this is very commonly present.

173. The barium ion, with carbonates soluble in water, gives a white precipitate of barium carbonate, BaCO_3 . In very dilute solutions it appears only after heating to boiling. It is soluble in most acids except sulphuric. No precipitate is produced with the free carbonic acid.

Oxalic Acid, $\text{H}_2\text{C}_2\text{O}_4$, and Oxalates (the Oxalate Ion)

The acid is a white solid, readily soluble in water and crystallizing from its solution with two molecules of water of crystallization. It has an intensely sour taste and is strongly acid to litmus.

174. Pure oxalic acid volatilizes without leaving a residue when heated on a platinum foil, giving irritating fumes. Oxalates of the non-volatile bases treated in the same manner are partly vaporized, but leave a residue behind, the carbonate of the base.

175. When heated nearly to boiling with concentrated sulphuric acid the solid oxalic acid or an oxalate is decomposed yielding carbon dioxid and carbon monoxid. The former can be identified by the turbidity which it produces in lime-water and the latter by the bright blue flame when it is ignited. Oxalic acid is not blackened by concentrated sulphuric acid.

For reactions of the oxalate ion ammonium oxalate may be employed.

176. The barium ion precipitates from neutral solutions

of the oxalates white, pulverulent, barium oxalate, BaC_2O_4 . It is insoluble in acetic acid. It dissolves in hydrochloric acid and is reprecipitated from this by ammonia. The calcium ion gives a similar result, even in very dilute solutions.

177. Potassium permanganate solution is quickly decolorized when warmed with oxalic acid or one of its salts, after acidifying with sulphuric acid. This is because of the strong reducing power of the acid. For the same reason an acidified solution of potassium dichromate is likewise reduced to a green chromic salt.

Chromic Acid, H_2CrO_4 , and Chromates (the Chromate Ion)

Chromic anhydrid, CrO_3 , when dissolved in water forms chromic acid, which only exists in solution. The acid and the chromates are all colored red or yellow. The normal chromates like K_2CrO_4 which contain two univalent metallic atoms to each acid radical, are yellow, but upon acidifying they become reddish by the abstraction of a part of the base and the formation of bichromates, also called dichromates, like $\text{K}_2\text{Cr}_2\text{O}_7$. Chromic anhydrid and chromates act as oxidizing agents, the chromium taking a positive charge and becoming the positive element of the product, if free mineral acids are present.

For the reactions use a 2-per-cent. solution of potassium dichromate.

178. The barium ion precipitates from solutions of chromates yellow barium chromate, BaCrO_4 , insoluble in acetic but soluble in hydrochloric acid.

179. The lead ion precipitates lemon-yellow lead chromate, PbCrO_4 , soluble with difficulty in nitric acid, readily soluble in sodium hydroxid.

180. The sulphid ion slowly changes an acidified solution of a chromate to brown, then green, chromic salt, without pre-

cipitation. If the solution is alkaline there is precipitated upon warming bluish-green chromic hydroxid, $\text{Cr}(\text{OH})_3$.

181. Concentrated hydrochloric acid evolves chlorine when warmed with a chromate, the chromium changing from the anion to the cation. The color of the solution is changed from yellow to green.

182. Alcohol or oxalic acid is oxidized by a solution of potassium dichromate acidified strongly with sulphuric acid, the chromium changing as in the preceding test and, consequently, the color of the solution being changed to green.

Boric Acid (Boracic Acid), H_3BO_3 , and Borates (the Borate Ion)

The free acid is a white, crystalline solid, soluble in water. It reddens litmus-paper and turns to a reddish-brown paper which has been colored yellow by a solution of turmeric. It is somewhat volatile with boiling water or alcohol and when the latter is ignited it imparts a green border to the flame. The borates of metals except those of the alkalis are insoluble in water, but soluble in most acids.

For the reactions a 2-per-cent. solution of borax may be used.

183. The barium ion precipitates, except in dilute solutions, white barium borate.

184. A few grains of the solid moistened with a few drops of concentrated sulphuric acid in a porcelain dish will give a green-bordered flame when mixed with 2-3 c.c. of alcohol and the latter is set on fire, and stirred with a glass rod while burning. The free acid does the same without the addition of sulphuric acid (compare with 75).

• 185. Slightly acidify the solution of a borate with hydrochloric acid, dip into this a piece of turmeric paper and dry the latter at a gentle heat. It is turned reddish-brown. Moistening this with an alkali turns it bluish or greenish-black.

186. From a hot, concentrated solution of a borate hydro-

chloric acid precipitates free boric acid which separates in white crystalline scales.

Orthophosphoric Acid, H_3PO_4 , and Orthophosphates (the Orthophosphate Ion)

This is the most common acid of phosphorus and is the one which is meant when phosphoric acid is spoken of without any distinguishing prefix. Although it can be obtained in the crystalline form, it is very deliquescent, so that it usually appears as a liquid, thick and syrupy when concentrated. It has a strong acid reaction and taste.

For testing use a 2-per-cent. solution of sodium phosphate, Na_2HPO_4 .

187. The barium ion precipitates from solutions of phosphates white barium phosphate, BaHPO_4 , soluble in most acids except sulphuric. It does not produce this with solutions of the free acid.

188. Magnesia mixture (the clear solution produced by adding to magnesium sulphate, ammonium chlorid, then making it alkaline with ammonium hydroxid) precipitates from solutions of phosphates white ammonium magnesium phosphate, NH_4MgPO_4 . Under the microscope it is seen to be in the form of snowflake-shaped crystals. The compound is soluble in acids. In dilute solutions the precipitation is slow and is favored by shaking or stirring.

189. If 0.5 c.c. of a solution of the phosphate ion is added to 5 c.c. of ammonium molybdate in nitric acid and the mixture slightly warmed, a yellow precipitate of ammonium phosphomolybdate, $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_{10}, 2\text{H}_2\text{O}$ forms slowly. It is easily soluble in ammonium hydroxid, and its formation is hindered by the presence of chlorids and of some organic compounds.

190. From solutions of phosphates containing no free acid, the ferric ion precipitates yellowish-white, gelatinous ferric

phosphate. If a little mineral acid is present, it can be removed by the addition of a few crystals of sodium acetate. An excess of the ferric ion should then be avoided as it produces reddish ferric acetate.

191. A solution of egg-albumin is not precipitated by orthophosphoric acid nor by solutions of orthophosphates acidified with acetic acid.

Metaphosphoric Acid, HPO_3 , and Metaphosphates (the Metaphosphate Ion)

The free acid is a transparent, ice-like solid, readily soluble in water. Boiling in water changes it into orthophosphoric acid. The solution when mixed with zinc oxid yields a plastic mass which hardens on standing.

A 2-per-cent. solution of sodium metaphosphate can be used for testing.

192. The barium ion precipitates from neutral solutions barium metaphosphate, $\text{Ba}(\text{PO}_3)_2$, soluble in hydrochloric acid.

193. Magnesia mixture (188) with the metaphosphate ion gives no precipitate that is insoluble in ammonium chlorid.

194. The molybdate ion also fails to form a precipitate.

195. Free metaphosphoric acid, or solutions of metaphosphates when acidified with acetic acid, will precipitate a solution of egg-albumin. (Difference from orthophosphoric acid.)

Hypophosphorous Acid, HPH_2O_2 , and Hypophosphites (the Hypophosphite Ion)

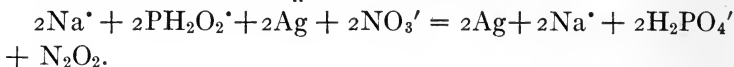
The hypophosphites are nearly all soluble in water. By heating the dry salts they are decomposed into phosphates and hydrogen phosphid, PH_3 , a combustible gas which before burning has the odor of decaying fish.



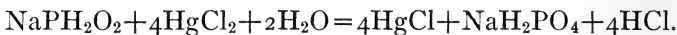
Oxidizing agents convert them into phosphates.

Use for the reactions a 2-per-cent. solution of NaPH_2O_2 .

196. The silver ion precipitates, first, white silver hypophosphite, AgPH_2O_2 , from which black metallic silver soon separates, the latter change being hastened by warming.



197. The mercuric ion from mercuric chlorid slowly forms white insoluble mercurous chlorid, HgCl , more rapidly on heating.



Long heating changes the color of the chlorid to gray from the separation of metallic mercury.

198. Hypophosphites readily decolorize a solution of KMnO_4 .

199. When warmed with concentrated sulphuric acid the hypophosphites cause an evolution of sulphurous oxid.

200. The barium and lead ions do not precipitate the hypophosphite ion.

All these reactions show the reducing power of the hypophosphite ion.

Thiosulphuric Acid, $\text{H}_2\text{S}_2\text{O}_3$, and Thiosulphates ("Hyposulphites") (the Thiosulphate Ion)

The acid does not exist free. Its salts are mostly soluble and act as reducing agents.

Sodium thiosulphate can be used for the reactions.

201. The silver ion produces a white precipitate of silver thiosulphate, $\text{Ag}_2\text{S}_2\text{O}_3$. It dissolves in an excess of the thiosulphate and is therefore not readily precipitated from concentrated solutions of the latter salt. When heated it turns black, silver sulphid being precipitated.

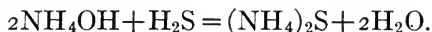
202. The barium ion precipitates white barium thio-sulphate, BaS_2O_3 , which is somewhat soluble in water.

203. Solutions of thiosulphates are decomposed by the mineral acids with an evolution of sulphurous oxid, sulphur being at the same time precipitated.

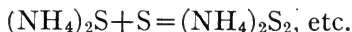
204. An acidified solution of potassium permanganate is immediately decolorized by a thiosulphate.

Hydrosulphuric Acid (Hydrogen Sulphide), H_2S , and Sulphids
(the Sulphid Ion)

Hydrosulphuric acid is a colorless gas with the odor of decaying eggs. It dissolves in about one-third of its volume of water at ordinary temperatures and this solution reddens litmus-paper. By the addition of alkaline hydroxids to this sulphids are formed.



Of its salts only those of the alkalies and alkaline earths are soluble in water. These, together with the sulphids of iron, manganese, and zinc evolve hydrogen sulphid when treated with sulphuric acid. The sulphids of some of the heavy metals like copper, mercury, and lead give sulphurous oxid instead. Solutions of the sulphids dissolve sulphur with the formation of the polysulphids—



For the reactions a 1-per-cent. solution of Na_2S or $(\text{NH}_4)_2\text{S}$ can be used.

205. The lead ion or silver ion with the sulphid ion form black precipitates of lead sulphid, PbS , or silver sulphid, Ag_2S .

206. Soluble sulphids when acidified with hydrochloric or sulphuric acid give hydrogen sulphid.



This can be identified by its odor or by its turning brown or black a paper previously dipped in a solution of lead acetate.

207. Polysulphids give the same gas when acidified, and also precipitate sulphur, very fine and nearly white.

208. Mercuric sulphid, lead sulphid, and some of the other insoluble sulphids yield no hydrogen sulphid when warmed with hydrochloric acid, but do so if at the same time a fragment of zinc is present.

**Hydroferrocyanic Acid, $\text{H}_4\text{Fe}(\text{CN})_6$, and Ferrocyanids
(the Ferrocyanid Ion)**

Use for the reaction a 1-per-cent. solution of $\text{K}_4\text{Fe}(\text{CN})_6$.

209. The ferric ion forms a deep blue precipitate of ferric ferrocyanid (55).

210. The copper ion produces a reddish-brown precipitate of copper ferrocyanid (73).

211. Ferrocyanids heated with concentrated sulphuric acid liberate carbon monoxid; with dilute sulphuric acid hydrocyanic acid, HCN , is set free. (Danger)

**Hydroferricyanic Acid, $\text{H}_3\text{Fe}(\text{CN})_6$, and Ferricyanids
(the Ferricyanid Ion)**

Use a 1-per-cent. solution of $\text{K}_3\text{Fe}(\text{CN})_6$ for the reactions.

212. The ferric ion with soluble ferricyanids gives no precipitate but turns the liquid brown (56).

213. The ferrous ion produces a deep blue precipitate with the ferricyanid ion (49).

**Sulphocyanic Acid, HSCN , and Sulphocyanates
(the Sulphocyanate Ion)**

A 1-per-cent. solution of KSCN may be used for testing.

214. The ferric ion forms a deep red liquid, but no precipitate, with sulphocyanates (57). It disappears upon the addition of mercuric chlorid.

**Hypochlorous Acid, HClO , and Hypochlorites
(the Hypochlorite Ion)**

A solution of NaClO may be used for the reactions.

215. Acidifying hypochlorites with hydrochloric acid sets hypochlorous acid or chlorine free. This can be recognized, if sufficient is present, by its color, odor, and bleaching moist litmus-paper.

216. Soluble hypochlorites bleach indigo solution—more rapidly after acidifying.

217. Hypochlorites do not bleach acid solutions of potassium permanganate.

218. The lead ion forms, first, a white precipitate which gradually becomes reddish, then brown from the formation of the dioxid, PbO_2 , for example,



Nitrous Acid, HNO_2 , and Nitrites (the Nitrite Ion)

NaNO_2 can be used for the reactions.

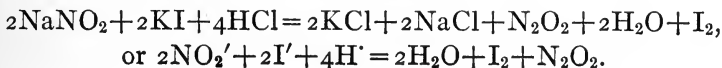
219. By acidifying solutions of nitrites, nitrous acid is set free. It is extremely unstable and is not used in the free state. From the solid salts or concentrated solutions a brown mixture of the oxids of nitrogen appears when acid is added.



220. The free acid or acidified solutions of its salts decolorize indigo solution upon heating.

221. Nitrites when acidified will decolorize potassium permanganate.

222. From a few drops of an iodid solution acidified with hydrochloric acid, nitrites set iodine free. Starch solution then gives a blue color with the iodine.



Ferric salts and a few other compounds, notably iodic acid, also decompose an iodide in a similar manner.

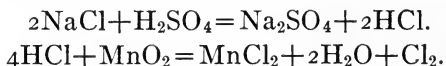
223. The silver ion forms silver nitrite, AgNO_2 , which is somewhat soluble in water, hence does not appear in dilute solutions.

Other reactions for minute amounts of nitrites are given under Water Analysis.

Hydrochloric Acid, HCl , and Chlorids (the Chlorid Ion)

Hydrochloric acid is a colorless gas with a suffocating odor, and very soluble in water, in which form it is commonly used. Most of its salts are also soluble in water.

224. Addition of concentrated sulphuric acid to the dry salts produces an evolution of hydrochloric acid gas. This has a strong odor and acid reaction. If manganese dioxide, potassium chlorate, or other oxidizing agent is also present chlorine is set free, recognizable by its color and odor.



A 1-per-cent. solution of NaCl will give the other reactions.

225. The silver ion precipitates white, curdy silver chlorid, AgCl , which, in very dilute solutions, remains for a long time in suspension. It is insoluble in nitric acid, but easily dissolves in ammonium hydroxid and can be reprecipitated from this solution by nitric acid. By exposure to sunlight the white compound turns violet, then nearly black.

226. The lead ion forms a white precipitate of lead chlorid, PbCl_2 , which dissolves in boiling water and, when this cools, separates again as white prismatic crystals.

Hydrobromic Acid, HBr , and Bromids (the Bromid Ion)

The free acid is similar to hydrochloric in physical as well as chemical properties. For the reactions use potassium bromid.

227. From a crystal of a dry bromid concentrated sulphuric acid liberates bromine upon warming. This is seen

as a reddish-yellow gas, most plainly by looking down into the test-tube. The addition of a little manganese dioxid increases the evolution of the gas. Nitric acid also sets free bromin from most bromids when it is heated; if it is in a solution it colors the liquid yellow. From a solution of a bromid, chlorin water liberates free bromin and this, when shaken with a drop of chloroform, dissolves giving the chloroform a brown color.

228. The silver ion precipitates from solutions of bromids, even when dilute, yellowish-white, curdy silver bromid, AgBr . It does not dissolve in nitric acid and is soluble with some difficulty in ammonium hydroxid.

Hydriodic Acid, HI , and Iodids (the Iodid Ion)

The acid resembles, physically and chemically, hydrochloric and hydrobromic acids.

229. A small crystal of the dry salt is decomposed by heating with concentrated sulphuric acid, iodine being evolved and volatilized as a deep purple vapor. Yellow nitric acid produces the same effect when boiled with the salt even in comparatively dilute solutions. A very slight amount of this vapor turns to a deep bluish-black a paper moistened or sized with starch solution.

A 1-per-cent. solution of potassium iodid may be used for the wet reactions.

230. From a solution of an iodid, bromine water or chlorine water sets free iodine which gives a dark blue color to a solution of starch. An excess of the chlorine water destroys the color. Iodids alone do not color the starch.

231. The silver ion precipitates the iodid ion as yellowish silver iodid, AgI , insoluble in nitric acid and nearly insoluble in ammonium hydroxid.

Hydrocyanic Acid, HCN , and Cyanids (the Cyanid Ion)

The free acid is a colorless liquid, very volatile, with the odor of bitter almonds, and extremely poisonous. The gas

burns with a violet flame. The cyanids of the alkalies and alkaline earths are soluble in water. Weak acids, including carbonic, liberate the acid from these, but not from all cyanids. The insoluble cyanids of the heavy metals form soluble cyanids with those of the alkalies, consequently potassium cyanid dissolves most of the former class.

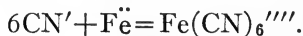
Use for the reactions a 1-per-cent. solution of KCN.

232. The silver ion forms a white precipitate of silver cyanid, AgCN , which is insoluble in nitric acid and but slightly so in ammonium hydroxid, but is soluble in KCN, forming $\text{KAg}(\text{CN})_2$, the potassium salt of the complex ion $\text{Ag}(\text{CN})_2'$.

233. A few drops of ferrous sulphate solution with a solution of a cyanid is converted by warming, after making alkaline with sodium hydroxid, into the ferrocyanid.



That is, the ferrous ion unites with the cyanid ion to form the complex ferrocyanid ion.



Upon acidifying with hydrochloric acid and adding a few drops of ferric chlorid (the latter is unnecessary if the ferrous sulphate contained any ferric salt), a deep blue color appears (55).

234. Acidification of solutions of cyanids evolves the free hydrocyanic acid, recognizable from its odor. From its poisonous nature it is dangerous to inhale more than a very little. Concentrated sulphuric acid decomposes the insoluble cyanids in the same manner.

Nitric Acid, HNO_3 , and Nitrates (the Nitrate Ion)

235. The free acid is a colorless liquid, very strongly corrosive. It colors protein compounds, like horn, feathers, quill toothpicks, etc., a bright yellow.

Almost all nitrates are soluble in water and all are decomposed with the evolution of oxygen when heated to a red heat.

KNO_3 can be used for the reactions.

236. At high temperatures they give up their oxygen to oxidizable substances like charcoal, causing deflagration. A few crystals dropped on a piece of red-hot charcoal will illustrate this.

237. In a narrow test-tube place 3-4 c.c. of a solution of a nitrate, then holding it in a slanting position slowly pour in as much concentrated sulphuric acid. The two liquids do not mix. If much heat is generated cool it by holding the tube in running water; then add a few drops of a concentrated solution of ferrous sulphate. A brownish-purple ring forms at the junction of the liquids. With minute amounts of the acid this appears only slowly.

238. Nitric acid heated with metallic copper (or nitrates with this and in addition a few drops of concentrated sulphuric acid) liberates nitric oxide which produces a brownish gas in the upper part of the test-tube.

239. Nitric acid or a solution of a nitrate acidified with hydrochloric acid will decolorize indigo on warming. It should, however, be remembered that chlorine and some other oxidizing agents will do the same.

Other more sensitive tests for minute amounts of nitric acid are given under the subject of Water Analysis.

Chloric Acid, HClO_3 , and Chlorates (the Chlorate Ion)

The free acid is not used. Its salts are active oxidizing agents yielding oxygen more easily than the nitrates. They deflagrate on red-hot charcoal.

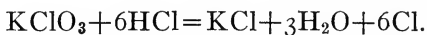
Use KClO_3 for the reactions.

240. Chlorates give no precipitate with the silver ion, but when heated on platinum foil they lose all their oxygen, be-

coming converted to chlorids which then react with the above reagent (225).

241. Concentrated sulphuric acid warmed with a fragment of a dry chlorate liberates chlorin tetroxid, ClO_2 , a greenish-yellow explosive gas. It is dangerous to use large amounts of substance or to heat rapidly.

242. Hydrochloric acid will evolve chlorin when warmed with a chlorate, as is proved by the characteristic color and odor.



Some oxids of chlorin may also be formed. The liquid then destroys the blue color of an indigo solution.

Acetic Acid, $\text{CH}_3\text{CO}_2\text{H}$, and Acetates (the Acetate Ion)

The free acid is a colorless liquid with a sharp odor and sour taste. It is easily volatile and its vapor is combustible. Most of its salts are decomposed by heating to a red heat, the residue being black. But few acetates are insoluble.

A 2-per-cent. solution of $\text{CH}_3\text{CO}_2\text{Na}$ may be used for the reactions.

243. A dry acetate heated with dilute sulphuric acid, or a solution of an acetate heated with concentrated acid evolves acetic acid which distils with the characteristic odor.

244. If in the above test a cubic centimeter of alcohol is added before heating, acetic ether (ethyl acetate) is produced, and this can be identified by its agreeable, fruity odor.

245. The ferric ion imparts a deep red color to solutions of neutral acetates or to acetic acid when the mixture is nearly neutralized by ammonium hydroxid. Boiling this precipitates the ion. Acidifying with hydrochloric acid turns it yellow (57).

Tartaric Acid, $C_2H_4O_2(CO_2H)_2$, and Tartrates (the Tartrate Ion)

Tartaric acid is a white crystalline solid, with an acid taste, easily soluble in water.

Tartrates prevent the precipitation by the alkaline hydroxids of copper, iron, and some other bases ordinarily precipitated thus.

$C_2H_4O_2(CO_2)_2KNa$ may be used for the reactions.

246. Dry tartaric acid or the tartrates are charred when warmed with concentrated sulphuric acid. Both it and its salts are decomposed when highly heated dry, the residue being black and the decomposition attended by an odor similar to that of burnt sugar.

247. The barium ion precipitates from solutions of tartrates white barium tartrate, $BaC_4H_4O_6$, soluble in ammonium salts or hydrochloric acid.

248. From solutions of tartrates the silver ion precipitates white silver tartrate, $Ag_2C_4H_4O_6$. If this is boiled black metallic silver separates. By dropping into the white precipitate before boiling enough ammonium hydroxid to dissolve it, then slowly warming it in a test-tube that has been thoroughly cleaned with sodium hydroxid and water, the silver deposits as a mirror on the tube. The heating may be accomplished by setting the tube in a beaker of hot water.

Citric Acid, $C_3H_5O(CO_2H)_3$, and Citrates (the Citrate Ion)

The free acid is a crystalline, colorless solid containing one molecule of water of crystallization. It is efflorescent, readily soluble in water and has an acid taste. When heated it melts, and afterward decomposes with blackening and the production of an odor, which, however, is different from that from tartaric acid. In the presence of citrates the alkaline hydroxids fail to precipitate iron and many of the other bases.

$K_3C_6H_5O_7$ may be used for the reactions.

249. Citric acid and its salts are decomposed by hot concentrated sulphuric acid with carbonization.

250. The barium ion forms a white precipitate of barium citrate, $\text{Ba}_3(\text{C}_6\text{H}_5\text{O}_7)_2$, in concentrated solutions. In dilute solutions it may not appear until after heating.

251. The silver ion precipitates white silver citrate, $\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$, but this does not reduce to metallic silver when it is warmed in the liquid.

The Identification of the Acids when Only One is Present

As a preliminary test warm 2 c.c. of concentrated sulphuric acid nearly to boiling in a test-tube, then drop in a piece of the powdered dry substance as large as a pea. Avoid heating to the boiling-point of the sulphuric acid. Notice whether there is an evolution of gas as shown by the formation of bubbles in the hot liquid.

A. A Colorless Gas is Evolved

Chlorids give HCl (odor).

Cyanids give HCN (odor). (Danger!)

Carbonates give CO_2 .

Nitrates give HNO_3 (odor).

Sulphites give SO_2 (odor).

Hypophosphites give SO_2 (odor).

Sulphids give H_2S (odor), although some sulphids of the heavy metals evolve SO_2 from hot sulphuric acid.

Ferrocyanids, ferricyanids, and sulphocyanates give a mixture of gases, sometimes HCN . (Danger!)

Thiosulphates give SO_2 (odor).

Acetates give acetic acid (odor).

Oxalates give CO and CO_2 .

Some salts of organic acids liberate colorless gases.

B. A Colored Gas is Evolved

Iodids give HI and iodine (violet).

Bromids give HBr and bromine (reddish-brown).

Nitrates give HNO_3 with oxids of nitrogen (brown or yellowish-brown).

Nitrites give oxids of nitrogen (yellowish-brown).

Chlorates give greenish-yellow oxids of chlorin (explosive).

Hypochlorites give hypochlorous acid or chlorin (suffocating odor).

C. No Gas is Evolved and No Blackening is Seen

Sulphates.

Phosphates.

Borates.

Chromates.

Arsenates.

Arsenites.

D. The Substance is Blackened

Many salts of organic acids as well as some organic compounds which are not salts are blackened by the strong sulphuric acid and in some cases colorless gases are set free.

If the preliminary test with sulphuric acid indicates the acid present, confirm it by the identification of its group, then by the reactions given under the acid.

In case the preliminary test does not give definite results, dissolve the substance in water if possible, if not in a very small amount of nitric acid. Determine the class to which the acid belongs, using separate portions of the solution for each test. To identify the acid after this has been done compare its reactions with those of all the acids of the class.

Although it is possible to group the acids in accordance with their similarities, the groups cannot be separated from each other and be afterward resolved into their components as easily as can the metals. Such an analysis is often accompanied with many difficulties. The following classification will aid in the identification of the acid radical of salts when

only one is present or, if there are several, provided they are not of the same group.

GROUP I

Precipitated by Ba in the presence of HNO_3 .

The sulphate ion, SO_4^{--} (sulphuric acid or sulphates).

GROUP II

Carefully neutralize the solution with NH_4OH if it is acid. If the cation is precipitated filter it out¹ and test the filtrate for the anion with BaCl_2 .² The anions of this group give a white or colored precipitate, soluble in HCl or HNO_3 . They are of two classes:

Class 1.—The substance evolves a gas with hot concentrated H_2SO_4 .

Carbonic acid, H_2CO_3 (carbonates).³

Sulphurous acid, H_2SO_3 (sulphites).³

Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$ (oxalates).

Citric acid, $\text{C}_6\text{H}_8\text{O}_7$ (citrates).

Class 2.—The compound does not evolve a gas with sulphuric acid.

Chromic acid, H_2CrO_4 (chromates).

Phosphoric acid, H_3PO_4 (orthophosphates).

Arsenic acid, H_3AsO_4 (arsenates).

Boric acid, H_2BO_3 (borates).

GROUP III

The anions of this group give precipitates with the silver ion in the presence of dilute HNO_3 . It contains four classes.

¹ Salts of acids in group II, except where the positive constituent is an alkali metal, are mostly insoluble in neutral or alkaline liquids. Both cation and anion will therefore in such cases be precipitated when the solution is neutralized.

² If the cation is one which will be precipitated by the chlorid ion (lead, silver, or mercurous), $\text{Ba}(\text{NO}_3)_2$ must be used instead of BaCl_2 .

³ Carbonates and sulphites which are insoluble in water cannot be dissolved in acid and the solution is tested with a barium solution. Why?

Class 1.—The precipitate with AgNO_3 turns black at once or on warming. Much HNO_3 prevents this.

The thiosulphate ion, $\text{S}_2\text{O}_3''$ (thiosulphuric acid, or thiosulphates, sometimes called “hyposulphites”).¹

The sulphid ion, S'' (hydrosulphuric acid, or sulphids, including polysulphids).

The hypophosphite ion, $\text{PH}_2\text{O}_2'$ (hypophosphorous acid, or hypophosphites).

Class 2.—These anions give a red or blue color with ferrous or ferric ions.

The sulphocyanate ion, SCN' (sulphocyanic acid or sulphocyanates or “sulphocyanids”).

The hydroferrocyanid ion, $\text{Fe}(\text{CN})_6''''$ (hydroferrocyanic acid, or ferrocyanids).

The hydroferricyanid ion, $\text{Fe}(\text{CN})_6'''$ (hydroferricyanic acid, or ferricyanids).

Class 3.—These anions bleach indigo solution at once or on warming.

The hypochlorite ion, ClO' (hypochlorous acid, or hypochlorites).

The nitrite ion, NO_2' (nitrous acid, or nitrites).

Class 4.—Belong to none of the first three classes.

The chlorid ion, Cl' (hydrochloric acid, or chlorids).

The bromid ion, Br' (hydrobromic acid, or bromids).

The iodid ion, I' (hydriodic acid, or iodids).

The cyanid ion, CN' (hydrocyanic acid, or cyanids).

GROUP IV

Give no precipitates with barium or silver ions in the presence of nitric acid.

The nitrate ion, NO_3' (nitric acid, or nitrates).

The chlorate ion, ClO_3' (chloric acid, or chlorates).

¹Since silver thiosulphate is soluble in an excess of thiosulphates it may not appear if too concentrated a solution of the thiosulphates is used.

The acetate ion, $\text{C}_2\text{H}_3\text{O}_2'$ (acetic acid, or acetates).

The tartrate ion, $\text{C}_4\text{H}_4\text{O}_6''$ (tartaric acid, or tartrates).

Practical Exercises on the Acids and their Salts

Determine the composition of the unknown compounds furnished by the instructors looking up their physical and chemical properties, their manufacture, their uses, etc. If a negative result is obtained in the examination for a metal the substance may be an uncombined acid. If the examination fails to show any acid it may be an oxid or a hydroxid. The hydroxids of the alkalies and alkaline earths form alkaline solutions in water; the others are insoluble. All but the hydroxids of the alkalies are decomposed to water and an oxid when heated in a dry tube. The oxids do not yield water on heating. All are insoluble in water except those of the alkalies and alkaline earths which dissolve as hydroxids. The peroxids and a few others, like those of mercury, give off oxygen when heated.

Questions for Further Study on the Reactions of the Acids

Where is any practical use made of the affinity of concentrated sulphuric acid for water? In diluting the acid which is the safer, to add the acid to the water or to add the water to the acid? Will the concentrated acid char such an organic compound as alcohol by removing the elements of water? What gas is evolved when a metal dissolves in sulphuric acid? Does it make any difference whether the acid is concentrated or dilute? Is it a compound of sulphuric acid which is precipitated from the aromatic acid when it is diluted with water? What cations are precipitated by the sulphate ion? Why is sulphuric acid selected for making the preliminary test?

Why is it not in all cases the weaker acid which is thus liberated?

Why do the sulphites so often contain sulphates? What effect do sulphites have on solutions of salts of which there are two classes, the *ous* and *ic*, like the mercurous and mercuric, ferrous and ferric, arsenous and arsenic? Will other acids than sulphuric set free the sulphurous acid from its salts? What is the chemical action of sulphurous acid upon potassium permanganate or the chromates? What is the chemical action by which hydrogen sulphid can be produced from sulphurous acid and its salts, and what is the active agent?

With solutions of what metals are soluble carbonates incompatible because of the precipitation of the former? Are carbonates ever decomposed by salts which have an acid reaction or only by free acids? What compound is formed when carbon dioxid acts upon lime-water? What would be the effect of a large excess of the gas? How are the bicarbonates produced and why are they so called? What application is made of the easy decomposition of the bicarbonates?

What is the physiological action of oxalic acid or the soluble oxalates? Are many of the other organic acids volatilized by heat without discoloration? What is meant by "reducing power"? After barium oxalate has been dissolved in hydrochloric acid, why is it precipitated unchanged by adding ammonium hydroxid?

What would be the objection to triturating a dichromate with tannic acid or sugar? Why does a solution of a dichromate turn from red to yellow when it is made alkaline? For what is chromic anhydrid used? What is the difference between a salt of chromic acid and a chromium salt?

How are the two phosphoric acids made? Will soluble phosphates be incompatible with other cations than iron, magnesium, and calcium? The phosphates of which metals

are soluble in water? Will acids and alkalies increase or decrease the solubility of phosphates? What is the commercial name of metaphosphoric acid? Which phosphoric acid is official in the U.S.P.? How much of the hydrogen of orthophosphoric acid can be replaced by metals to form salts? How much in hypophosphorous acid? How can a mineral acid be removed from a solution by adding sodium acetate (190)? How do salts of phosphoric acid formed by replacing varying amounts of hydrogen differ from each other? What use is made of the zinc compounds of metaphosphoric acid? What property of the hypophosphites accounts for their decolorizing a permanganate solution? What is the chemical change which occurs when hypochlorites decolorize indigo solution? What is the change in nitrites when they decolorize a permanganate solution? Is their chemical action always of this kind when mixed with other compounds? Is the chemical nature of the organic nitrites used medicinally the same as of the inorganic salts? Is the chemical activity of nitrites different in acidified solutions from that of neutral or alkaline solutions?

What metallic salts of the halogens are insoluble in cold water? What is the effect of strong oxidizing agents on hydrochloric acid? How do the compounds of chlorine, bromine, and iodine compare with one another in stability as shown in their decomposition by the free halogens and by other agents? What is the action of their salts on the alkaloids? What substances liberate iodine from iodides and are therefore incompatible with these?

In what combination does hydrocyanic acid occur in plants and is it always poisonous in such form? To what extent does it ionize? In what plants is it found? How stable are solutions of the acid or its salts? Are any of the salts poisonous? What are the most common compounds which may be oxidized by nitric acid? Does it ever cause explosions thus or

form explosive compounds? What is its action upon alkaloïds? What is the origin of the yellow color frequently seen in nitric acid? Are the nitrates chemically similar to the free acid? How do the properties of the chlorates compare with those of the nitrates? With what class of substances are dry chlorates incompatible and why?

What change is produced upon the tartrates by oxidizing agents and what is the effect upon the latter? Where are tartrates and citrates used to prevent the precipitation of cations by the alkalies?

CHAPTER III

ORGANIC COMPOUNDS

Benzin and Petroleum Ether

THESE are mixtures of hydrocarbons of the marsh-gas series, boiling between 55° and 75° . They do not crystallize by cooling to 0° , and are insoluble in water.

252. If dropped into a cooled mixture of one part concentrated sulphuric acid and three parts fuming nitric acid there is no discoloration or odor of bitter almonds.

253. Iodin dissolves in either to a violet solution.

Benzene (Benzol), C_6H_6

A colorless liquid with a characteristic odor, boiling at about 80° , lighter than water and almost insoluble in it. At zero it solidifies to a crystalline mass.

254. Cool a mixture of concentrated sulphuric and nitric acids, 5 c.c. of each, as with benzin (252) and slowly drop in 15–20 drops of benzene, keeping the liquid cool. Nitrobenzene $C_6H_5NO_2$, is formed, a yellowish oil with the bitter almond odor.

255. Iodin dissolves in benzene to a blood-red solution.

Chloroform, $CHCl_3$

A colorless, neutral liquid with characteristic odor, having a specific gravity of 1.5 and a boiling-point of about 61° . It is almost insoluble in water.

256. A strip of filter-paper moistened with chloroform burns with a green-edged, yellow flame.

257. A drop of chloroform should not be rendered milky by a drop of silver nitrate (225).

258. With several times its volume of alcohol and a few

drops of sodium hydroxid it is decomposed by warming into salts of hydrochloric and formic acid.



This solution gives a white precipitate with silver nitrate after acidifying with nitric acid (225).

259. To a solution of potassium hydroxid in alcohol add a drop of anilin and one of chloroform and warm gently. Phenyl carbylamin, isonitril, or isocyanid, $\text{C}_6\text{H}_5\text{NC}$, is formed, recognizable by its offensive odor.

260. With a few crystals of beta-naphthol and a few drops of sodium hydroxid chloroform gives a blue color when warmed slightly. When only a minute quantity is present the blue may be transient.

261. In a 10 c.c. dry test-tube place 5 c.c. of chloroform and add without agitation 5 c.c. of perfectly clear barium hydroxid solution. After the corked tube has stood six hours in a dark place there should be no turbidity at the line of contact of the liquids (absence of decomposition products in chloroform which is otherwise pure).

262. Sodium hydroxid with a few drops of copper sulphate (Trommer's reagent) gives a reddish-yellow precipitate when warmed with a drop of chloroform.

263. When shaken with one-tenth its volume of concentrated sulphuric acid and allowed to stand, pure chloroform is not colored yellow or brown.

264. When pure chloroform has been thoroughly shaken with an equal volume of water the latter, after pouring off, does not affect litmus-paper, is unchanged with silver nitrate, and gives no color with a few drops of potassium iodid and starch solution (230).

Iodoform, CHI_3

Yellow crystals with a characteristic odor. It is almost insoluble in water, but dissolves in alcohol or ether.

265. A drop of the alcoholic solution allowed to evaporate on a microscope slide leaves the iodoform in flat, hexagonal or star-shaped crystals, as is shown by the microscope.

266. The dry substance when heated in a test-tube melts at about 115° to a brown liquid and afterward gives off the violet vapors of iodine, leaving a charred mass. The latter is completely combustible on a platinum foil.

267. Water which has been shaken with one-fifth its weight of pure iodoform and filtered is colorless, neutral, has no bitter taste and is unaffected by silver nitrate.

Ethyl Alcohol, C_2H_5OH

A colorless, neutral liquid with a specific gravity of 0.79 and a boiling-point of 78° .

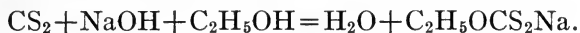
268. 1 c.c. of alcohol with an equal volume of concentrated sulphuric acid and a few crystals of sodium acetate gives, when heated to the boiling-point, ethyl acetate, $C_2H_5-C_2H_3O_2$ (acetic ether), which distills with a pleasant, fruity odor.

269. With enough sodium hydroxid to make it alkaline, then a solution of iodine in potassium iodid until it has a yellow color, followed by gentle warming, there forms, immediately or after standing, a light yellow precipitate of iodoform (page 123). This reaction is a very sensitive one. It is also given by acetone, acetic aldehyde, and some other organic compounds, but not by methyl alcohol.

270. If enough potassium dichromate is added to color the alcohol light yellow, and if it is then acidified quite strongly with sulphuric acid it is reduced to a chromic salt by boiling and this colors the liquid green. This is not characteristic of alcohol, as other reducing agents may produce the same effect.

271. 10 or 12 drops of alcohol with 2 or 3 of carbon bisul-

phid and a little concentrated sodium hydroxid produce a yellow sodium xanthogenate.



This with an aqueous solution of ammonium molybdate(1:10), after acidifying with sulphuric acid, gives a red color. To obtain it with dilute alcoholic solutions a few drops should be well mixed with one of carbon disulphid and a very small piece of sodium hydroxid or potassium hydroxid; after standing in an evaporating dish at the ordinary temperature until the carbon disulphid has disappeared a drop of the ammonium molybdate is to be added and enough sulphuric acid to acidify.

272. Pure alcohol (U.S.P.) should mix with water, ether, and chloroform without cloudiness. It does not affect the color of litmus-paper and leaves no residue upon evaporation; if it evaporates spontaneously from a paper no foreign odor should be perceptible. With half its volume of potassium hydroxid solution it should not at once become dark colored nor should silver nitrate give more than a faint opalescence nor more than a faint brownish tint when standing six hours in diffused daylight.

273. To test for methyl alcohol in ethyl alcohol dilute the liquid if necessary with water so that it contains no more than 10 per cent. alcohol; make a spiral 7 mm. thick and 30 mm. long by winding clean copper wire around a glass rod; place 10 c.c. of the alcohol in a 30-40 c.c. test-tube and plunge into it the spiral, heated to redness, repeating the operation five or six times and keeping the liquid cool by placing the tube in water. Filter and boil gently until no odor of acetaldehyd remains. Cool and add one drop of a 5-per-cent. solution of resorcin, then pour it carefully on to concentrated sulphuric acid in a narrow test-tube so that the two do not mix. After two or three minutes rotate the tube slowly. More than 2 per cent. of methyl alcohol gives a rose-red ring at the line of contact.

Amyl Alcohol, $C_5H_{11}OH$

A colorless liquid with a specific gravity of 0.82, and a boiling-point of 131° . It dissolves in alcohol but not in water. It has a peculiar odor, its vapor causing coughing.

274. In alcoholic fluids any considerable quantity of amyl alcohol can be detected by means of its odor by pouring into a large beaker, spreading it over the sides, and causing the ethyl alcohol to evaporate quickly by swinging through the air. Evaporation on a water-bath also removes the water and ethyl alcohol and leaves the amyl alcohol.

275. If hydrochloric acid is dropped into a 1-per-cent. solution of methyl violet until it becomes green, then amyl alcohol is mixed with it in a porcelain dish, there appear on the top of the liquid violet drops.

276. Amyl alcohol dropped into 1 c.c. of concentrated sulphuric acid gives a red color.

Glycerin, or Glycerol (C_3H_5OH)₃

A neutral, colorless, odorless, syrupy liquid of a specific gravity of 1.25 to 1.27, with a sweet taste. It is hygroscopic and dissolves in water or alcohol.

277. A borax bead dipped in a solution which contains glycerol colors the blue flame of the Bunsen burner green (184).

278. Glycerol prevents the precipitation of copper, lead, or ferric solutions by the alkaline hydroxids.

279. Five drops each of glycerol and concentrated sulphuric acid gently warmed with as much resorcin as can be taken up on the point of a knife-blade gives first a crimson, then a blood-red color. Too high heat causes charring. When diluted with 5 cc. of water and made alkaline with ammonium hydroxid the yellow solution shows a green fluorescence.

280. Pure glycerol will give no precipitate when tested by Trommer's test (262).

281. Pure glycerol when warmed gently with an equal

volume of concentrated sulphuric acid or sodium hydroxid is not colored dark.

282. An ammoniacal solution of silver nitrate is not changed when warmed with pure glycerol, but upon the addition to it of sodium hydroxid black metallic silver separates immediately.

Phenol (Carbolic Acid), C_6H_5OH)

Pure phenol is a colorless, crystalline solid with a characteristic odor. It melts at about 40° and dissolves in water to a neutral solution. The melted phenol solidifies upon cooling, but the addition of a little water prevents this. An aqueous solution may be used for testing.

283. Neutral ferric chlorid solution, not in excess, produces a deep violet color which is changed to a yellow with hydrochloric acid.

284. Bromin water precipitates first white, then yellow tribromphenol, $C_6H_5Br_3OH$, soluble in alkaline hydroxids or hydrochloric acid.

285. A solution of phenol in water made alkaline with a drop of ammonium hydroxid becomes blue when warmed with a few drops of bromin water.

286. Five c.c. of an aqueous solution boiled with 5 or 6 drops of concentrated nitric acid forms a brownish or yellow compound, picric acid, $C_6H_2(OH)(NO_2)_3$, which colors a large amount of water. The color is intensified by making it alkaline with ammonium hydroxid.

287. A phenol solution with a drop of anilin, then an excess of a solution of calcium hypochlorite gives a deep blue color. (Anilin and calcium hypochlorite give a red.)

Creosote

This is a colorless or yellowish liquid with a smoky odor, not solidifying in the cold and but slightly soluble in water.

288. Ferric chlorid colors the aqueous solution a transient

violet-blue passing into a grayish-green and brown, lastly a brown precipitate.)

289. Bromin water gives a brownish precipitate.

Formaldehyd (Formalin), HCHO

A colorless gas with a very irritating odor. It dissolves in water and is commonly to be obtained in the form of a 40-per-cent. solution. By concentrating the aqueous solution the aldehyd becomes converted into the solid paraformaldehyd $(\text{HCHO})_3$.

A 1-per-cent. solution can be used for the tests.

290. The silver ion to which enough ammonium hydroxid has been added to dissolve the precipitate first formed is reduced by formaldehyd to metallic silver when allowed to stand several hours in a dark place, the metal being deposited as a mirror. If warmed this occurs immediately.

291. Formaldehyd reduces a solution of cupric sulphate made alkaline with sodium hydroxid with the formation of a reddish-yellow precipitate of cuprous oxid (Trommer's reaction).

292. To a dilute fuchsin solution acidified with sulphuric acid add just enough sodium sulphite to decolorize it. Formaldehyd produces a purplish-violet color when warmed with this.

293. Formaldehyd gives a yellowish precipitate when it is warmed with phenyl-hydrochlorid; this is the hydrazone $\text{C}_6\text{H}_5\text{NHNCH}_2$.

294. A few cubic centimeters of a dilute formaldehyd solution with about 50 mg. of resorcin and half its volume of 50-per-cent. sodium hydroxid, when warmed, is turned first yellow, then red. It is a very sensitive test.

295. Ammonium hydroxid converts a solution of formaldehyd in solution into hexa-methylen-tetra-amin, which remains as a solid after evaporation.

296. A solution of 40-50 per cent. of sodium hydroxid and 5 per cent. of resorcin in water when boiled half a minute with an equal volume of a dilute formaldehyd solution gives a red color. Albuminous compounds prevent the reaction.

297. Fifteen c.c. of a very dilute solution of formaldehyd with 1 c.c. of a dilute solution of phenyl-hydrazin hydrochlorid and a few drops of a freshly prepared solution of sodium nitroprussid when made alkaline with sodium hydroxid becomes blue; in milk a grayish-green color results. Chloroform gives a similar result, but only in a much stronger solution, where it can usually be identified by its odor.

If to the mixture of formaldehyd and the phenyl-hydrazin salt ferric chlorid is added, then the liquid strongly acidified with concentrated hydrochloric acid a red color forms, very slowly changing to orange-yellow.

If milk containing formaldehyd is diluted with an equal volume of water, then poured on to concentrated sulphuric acid in a test-tube so as to produce two layers, a violet ring appears between the liquids. This is Hehner's test.

These three last tests can be made on milk directly without distillation and all are very sensitive.

Chloral Hydrate, Hydrated Chloral, $\text{CCl}_3\text{CHO}, \text{H}_2\text{O}$

Colorless crystals with a sharp odor, soluble in water or alcohol to a neutral solution, melting at 57° and boiling at 98° .

298. When warmed with alkaline substances chloral hydrate is decomposed with the formation of chloroform. The latter may be detected by its odor or by the reactions for chloroform in the presence of an alkali (258, 259).

299. Chloral hydrate gives no precipitate with silver nitrate, but if it is allowed to stand for a time with dilute sulphuric acid and zinc, silver nitrate being subsequently added, silver chlorid is precipitated.

300. From an ammoniacal solution of silver nitrate chloral hydrate precipitates dark-brown metallic silver, slowly at the ordinary temperature, more rapidly on warming.

301. A chloral hydrate solution with as much resorcin as can be held on the point of a penknife and five drops of sodium hydroxid gives an intense red color which is destroyed by hydrochloric acid.

302. Chloral hydrate with ammonium sulphid gives an orange color then a brown, more quickly on warming.

303. Pure chloral hydrate should not give the iodoform reaction (269).

Benzoic Acid, $C_6H_5CO_2H$

Colorless needle-shaped or tabular crystals with an aromatic odor, melting at 121° , soluble with difficulty in cold water but easily in warm water, soluble in alcohol, ether, and chloroform.

304. When heated in a dry tube the crystals melt and volatilize without blackening, becoming condensed in the crystalline form on the cooler part of the tube.

305. Benzoic acid dissolves in sulphuric acid without charring.

306. The lead ion precipitates white lead benzoate, $Pb(C_6H_5CO_2)_2$, soluble in much boiling water and reprecipitated on cooling.

307. The ferric ion precipitates flesh-colored basic ferric benzoate, $Fe_2(C_7H_5O_2)_3(OH)_3$. Tartaric or citric acid prevents this.

Salicylic Acid, $C_6H_4OHCO_2H$

Colorless, odorless, needle-shaped crystals, only slightly soluble in cold water, more soluble in hot water. The normal salts are soluble in water, the basic ones less so. From these solutions the free acid is precipitated by mineral acids.

308. When slowly heated salicylic acid melts at 156° and

sublimes as white crystals; by rapid and high heating it decomposes into carbon dioxid and phenol, the latter recognizable by its odor.

309. The ferric ion gives a deep bluish-purple color. Mineral acids, soluble hydroxids and some salts may prevent the formation.

310. Salicylic acid, or the salicylates, dissolved in 1 c.c. of methyl alcohol, when 1 c.c. of concentrated sulphuric is added and the mixture warmed, will produce methyl salicylate, $C_6H_4(OH)(CO_2CH_3)$, oil of wintergreen. Ethyl alcohol gives ethyl salicylate in the same manner, having a very similar odor.

311. Salicylic acid gives similar reactions to phenol with boiling nitric acid (286), and bromin water (284).

312. Concentrated sulphuric acid makes a colorless solution with salicylic acid when cold, turning brown upon warming.

Meconic Acid, $C_5H_2O_3(CO_2H)_2$

313. Meconic acid is a white crystalline solid, soluble with difficulty in cold water, but readily so with warming, also soluble in alcohol.

314. The ferric ion imparts a blood-red color to a solution of meconic acid. This is not discharged by boiling (245), by acidifying with hydrochloric acid (245), nor by mercuric chlorid (214). Stannous chlorid decolorizes it.

315. The silver ion produces a yellowish precipitate, becoming a brighter yellow when it is warmed.

Tannic Acid or Tannins

There are a number of tannins with similar properties. They are yellowish powders, soluble in an equal weight of water, also in alcohol or glycerol, and turning litmus-paper red.

316. Solutions of tannic acid, when made alkaline, rapidly absorb oxygen, becoming red, brown, or black.

317. Ferric salts produce a blue-black color or precipitate which is prevented or destroyed by acids.

318. Lime-water produces a bluish-white precipitate, becoming darker blue as the amount of the reagent is increased, and finally changing to a pinkish color.

319. Tannic acid reduces a permanganate solution.

320. Solutions of albumin, gelatin, or starch are precipitated by tannic acid.

321. A solution of iodine in potassium iodide to which enough potassium cyanide has been added to produce a colorless liquid gives a red color with tannic acid. An excess of the cyanide deepens the color. It changes in one or two minutes to brown.

322. A solution of antimony potassium tartrate precipitates a tannic acid solution.

323. Tannic acid precipitates most alkaloids.

Gallic Acid, $\text{C}_6\text{H}_2(\text{OH})_3\text{CO}_2\text{H}$

A white or yellowish, crystalline powder, soluble in 100 parts of water, also in alcohol or glycerol. It has an acid reaction.

324. When made strongly alkaline solutions of gallic acid become yellow, red, and brown through the absorption of oxygen. If the alkali is not in excess the solution slowly turns green.

325. Ferric salts give a bluish-black color or precipitate with gallic acid solutions.

326. Lime-water gives a bluish precipitate, as the reagent is increased darker blue in color by reflected light and a greenish by transmitted light, with a large excess changing to a pink color.

327. A permanganate solution is reduced by gallic acid.

328. Solutions of albumin, gelatin, or starch are not precipitated by gallic acid.

329. Gallic acid does not precipitate the alkaloids.

330. With a solution of iodine in potassium iodide which has

been decolorized by potassium cyanid, gallic acid gives a red color, changing to yellowish-brown. The latter change is slower than with tannic acid (321).

Starch, $(C_6H_{10}O_5)_x$

It is found in vegetable substances in the form of granules, those of one species of vegetable often differing sufficiently from those of another to render possible determination of their source by microscopic examination. It is insoluble in cold water, neutral and tasteless. The granules are destroyed by heating with water, the starch forming a semi-soluble paste. This may be used for the tests.

331. With a solution of iodine starch gives a dark blue color. This is decolorized by alkalis or by heating. In the latter case when the liquid cools it becomes colored again. The dry starch is colored by the same reagent.

332. When boiled some time with a dilute mineral acid starch is converted into glucose, $C_6H_{12}O_6$. The liquid then forms no blue compound with iodine.

Glucose or Dextrose (Grape Sugar), $C_6H_{12}O_6$

This is to be obtained as a dry solid or as a colorless syrup. Its taste is less sweet than that of cane-sugar. It is readily soluble in water.

333. A solution of glucose when made alkaline with sodium hydroxid and into which copper sulphate has then been dropped gives on warming a reddish-yellow precipitate of cuprous oxid, Cu_2O (Trommer's reaction).

334. A glucose solution when heated 15 minutes with as much phenyl-hydrazin hydrochlorid as can be taken up on the point of a knife-blade and twice as much crystallized sodium acetate will, on cooling, deposit bright yellow crystals of phenyl-glucosazone, best observed with the microscope.

335. Mixed with a small piece of compressed yeast and

placed in an inverted test-tube, standing at a temperature of 40° with the mouth under some of the same solution, the glucose ferments to carbon dioxid, which rises in the tube and can be tested by lime-water (171). Alcohol (269) is formed at the same time.

336. When warmed with glucose an ammoniacal solution of silver nitrate is reduced with the deposition of metallic silver.

337. Concentrated sulphuric acid does not blacken dry glucose in the cold.

Saccharose (Cane-Sugar), $C_{12}H_{22}O_{11}$

Colorless, odorless, sweet crystals, neutral in reaction.

338. With Trommer's reagent (333) cane-sugar gives no precipitate by heating to the boiling-point, although it may do so by long-continued heating.

339. Boiling with dilute mineral acids changes cane-sugar into glucose which may be detected in the above manner after neutralizing (333).

340. With phenyl-hydrazin saccharose reacts like glucose (334).

341. An aqueous cane-sugar solution (1:10) when quickly heated to boiling with an ammoniacal solution of silver nitrate then allowed to cool should give no more than a faint coloration but no dark precipitate in five minutes.

342. Concentrated sulphuric acid turns dry cane-sugar yellow, brown, and at last black without the application of heat.

Lactose (Milk-sugar), $C_{12}H_{22}O_{11}$

White, hard crystals with a somewhat gritty, sweetish taste, less soluble in water than glucose or saccharose.

343. Lactose gives the same results as glucose with Trommer's reagent (333).

344. Yeast does not produce the fermentation of lactose (335).

345. Concentrated sulphuric acid in the cold does not blacken dry milk-sugar.

346. Lactose with phenyl-hydrazin (334) and Trommer's reagent (333) gives similar results to those obtained from glucose.

Antipyrin (Phenyl-di-methyl-pyrazolon), $C_6H_5(CH_3)_2C_3N_2HO$

Colorless, odorless crystals with a bitter taste. It unites with acids, as do the alkaloids, to form salts, but has no alkaline reaction to litmus. It melts at 113° and blackens at higher temperatures. It is precipitated by most of the general alkaloidal reagents (page 139).

347. Concentrated sulphuric acid dissolves antipyrin to a colorless solution, not darkened by heating.

348. A solution of antipyrin in water when made strongly acid with nitric acid and warmed turns yellow, then red (distinction from acetanilid and acetphenetidin).

349. The solution in water with a few drops of fuming nitric acid becomes emerald-green; with a larger amount of the acid it turns red. A nitrite added to a slightly acidified solution of antipyrin also gives the same green color.

350. The aqueous solution of antipyrin is colored red by a drop of ferric chlorid solution becoming yellow with sulphuric acid.

351. Mercuric chlorid gives a white precipitate, readily soluble on warming and reprecipitating as the solution cools.

Acetanilid (Antifebrin), $C_6H_5NHCH_3CO$

A colorless, odorless, nearly tasteless, crystalline substance, soluble with difficulty in cold water, but easily soluble in hot water or alcohol. It melts at 113° .

352. Acetanilid dissolves in either concentrated sulphuric or nitric acid without discoloration (347).

353. When heated with sodium hydroxid acetanilid is decomposed with a formation of anilin which gives its characteristic odor. If then a few drops of chloroform are added and the mixture heated it gives the disagreeable odor of isonitril (259).

354. One c.c. of hydrochloric acid warmed with a little acetanilid decomposes the latter into anilin and acetic acid. If a drop of phenol is added, and a little calcium hypochlorite solution, the liquid becomes reddish. When made alkaline with ammonium hydroxid this changes to a blue (indophenol reaction).

355. The ferric ion produces no color with acetanilid beyond the yellow of the reagent. When warmed this becomes darker.

356. Warmed with 1 c.c. each of concentrated sulphuric acid and alcohol the odor of ethyl acetate (268) appears.

Phenacetin (Para-acet-phenetidin), $C_2H_5OC_6H_4NHCH_3CO$

Colorless, odorless, almost tasteless crystals, soluble in hot water or alcohol, almost insoluble in cold water. It melts at 135° and sublimes at a higher temperature with white fumes.

357. Concentrated sulphuric acid does not discolor phenacetin.

358. Warmed with concentrated nitric acid a yellow or orange color appears.

359. Phenacetin does not give the isonitril reaction (259) except after long heating, as it decomposes much more slowly than acetanilid (353).

360. Phenacetin gives the indophenol reaction like acetanilid (354).

361. The ferric ion gives a yellow color on heating.

362. When heated with concentrated sulphuric acid and alcohol, phenacetin gives ethyl acetate (356).

363. 0.1 grm. of phenacetin warmed one minute with 1 c.c. of concentrated hydrochloric acid, then diluted to 10 c.c., on the addition of three drops of a solution of chromic anhydrid in water gives a ruby-red color.

• Salol (Phenyl Salicylate), $C_6H_4OHCO_2C_6H_5$

A colorless, crystalline powder with an aromatic odor, insoluble in water but soluble in alcohol. It melts at 42° ; in hot water it goes to the bottom in oily drops.

364. When warmed with water and a few drops of sodium hydroxid it dissolves with decomposition. From this solution hydrochloric acid precipitates the salicylic acid as a white solid and the phenol can be recognized by its odor.

365. Equal parts of salol and potassium nitrate mixed with 1 c.c. of concentrated sulphuric acid form a bright greenish-blue liquid. On dilution with water or through standing in the air it passes into red and fades. Sulphuric alone produces no change.

366. From the alcoholic solution bromin water precipitates white monobromsalol.

367. On adding to an alcoholic solution of salol a few drops of a very dilute (straw-yellow) solution of ferric chlorid a violet or purple color appears; if the salol solution is dropped into the iron solution there is a white precipitate but no color.

368. After shaking with water and filtering, the filtrate should give no result with the ferric ion (283, 309), the barium ion (164, 187), nor the silver ion (225).

Sulphonal (Di-ethyl-sulphon-di-methyl-methan),
 $(C_2H_5SO_2)_2C(CH_3)_2$

Colorless, odorless, tasteless crystals, soluble with difficulty in cold water, but readily by the aid of heat, also in alcohol. It melts at 126° .

369. On platinum foil sulphonal burns with a yellow flame and the odor of sulphurous oxid.

370. If sulphonal is mixed with ten times its bulk of powdered charcoal and the mixture heated to redness in a dry tube it gives off the garlicky odor of mercaptol. Acetic acid and sulphurous oxid are formed also. If instead of charcoal the sulphonal is fused with potassium cyanid mercaptol is formed and also potassium sulphocyanate, the latter being found in the aqueous solution by the use of the ferric ion after filtering(214).

371. Sulphonal is not decomposed by mineral acids, alkalies, nor the halogens.

The Alkaloids

The alkaloids are a class of vegetable nitrogenous compounds which are chemically similar to ammonia. Like this the free alkaloids are of a basic nature and they form salts by uniting with acids without the setting free of hydrogen. Only a few of the alkaloids are liquid, most of them, as well as their salts, being crystallizable solids. Their salts are, as a rule, much more easily soluble in water than the alkaloids themselves. They are decomposed by alkalies, the alkaloid being set free, just as ammonia is freed from its salts by the same reagents. When the solution is concentrated this process often results in their precipitation, as the alkaloid is less soluble than its salts. There is a great difference in the comparative solubility of the alkaloids in many of the organic liquids like chloroform, benzene, ether, petroleum ether, amyl alcohol, etc., and the methods devised for their separation are based upon this. They all have a bitter taste, as do their salts. The separation and identification of the alkaloids is not as simple an operation as that of the metallic compounds. It should be borne in mind that a very small amount of impurity may conceal or to a great degree modify the reactions.

There are a number of reagents which will precipitate most

or all of the alkaloids and these are of value in proving the presence or absence of the class, although the results are often so similar that they cannot be used for the identification of the individual members. Among the most important of these alkaloidal group reagents are:

Tannic acid, which precipitates most alkaloids, as well as some other similar substances, as white or yellowish, flocculent compounds. They are often soluble in excess of the precipitant or in other acids.

Picric acid, which from not too dilute solutions precipitates yellow compounds, often crystalline in form.

Phosphomolybdic acid precipitates the alkaloids and similar nitrogenous compounds in the form of yellowish or brownish-yellow solids. These can be filtered from the solution and the alkaloid set free from them by the alkalies and their carbonates.

Phosphotungstic acid acts like the phosphomolybdic in most cases.

Mercuric potassium iodid precipitates most alkaloids from solutions of their sulphuric or hydrochloric acid salts as white or yellow compounds.

Iodin in potassium iodid forms brown precipitates with alkaloidal solutions.

Mercuric chlorid, *platinic chlorid*, or *gold chlorid*, from not too dilute solutions, throw down white or yellowish precipitates. With dilute solutions they may only form a turbidity.

In order to identify a compound as an alkaloid it must not only give the general tests for the class but be characterized by some special reaction or reactions. In the special reactions that follow it may be assumed, unless it is otherwise stated, that the alkaloid under discussion will, in the main, give the general reactions.

In the reactions of the alkaloids and in others where it often becomes necessary to identify minute quantities of material

it is convenient, instead of test-tubes, to make use of small, rather flat watch-crystals. The results of the treatment of a drop of solution with one of the reagent are plainly perceptible if the watch-glass stands upon a suitably colored paper, and the precipitate can be examined with the microscope, placing the watch-glass upon the stage. If it is desired to make the test upon a solid compound the drops of solution on the watch-glass may be evaporated to dryness on the steam-bath. At first rather large amounts of the alkaloids may be used, but after some skill has been gained this should be reduced to very minute quantities in order to show the sensitiveness of the reagents.

Morphin, $C_{17}H_{19}NO_3$

Morphin and its sulphuric and hydrochloric acid salts are white compounds crystallizing in needles or prisms.

372. Concentrated nitric acid dissolves morphin or its salts with a blood-red color which gradually passes into a yellow. The latter is not changed to a violet by addition of stannous chlorid, but is colored reddish-brown. Only a small amount of the acid should be used (difference from quinin).

373. Concentrated sulphuric acid dissolves morphin to a colorless liquid. If to this a trace of nitric acid is added there is no change in color, but if it has stood 24 hours, or is heated to 100° for half an hour, the nitric acid produces a red. A crystal of potassium permanganate added to the concentrated sulphuric acid solution should produce no violet or purple color.

374. Fröhde's reagent gives a violet solution, gradually changing to brown, green, and yellow.

375. A neutral solution of ferric chlorid with morphin or solutions of its neutral salts gives a blue color. Only a small quantity of the ferric compound can be used, as an excess prevents the reaction. The color is destroyed by free acids and impurities may prevent its appearance. The ferric

chlorid, which ordinarily has an acid reaction, must be prepared by subliming the crystals in a hard-glass tube after driving off the water and acid by gentle heating; then dissolve the sublimate in distilled water. The solution should be nearly or quite neutral. Impurities may prevent the formation of the color. The correctness of the reagent must be proved by its ability to produce the blue with a specimen of pure morphin sulphate. Some ptomains give a greenish color, but not a blue. None of the other vegetable alkaloids give this result.

376. Morphin with half its weight of sugar gives a red color to a drop of concentrated sulphuric acid.

377. Vanadium sulphate produces a reddish, then a violet color.

Narcotin, $C_{22}H_{23}NO_7$

Concentrated sulphuric acid dissolves narcotin to a colorless liquid. If the acid contains a trace of nitric acid, as happens often with the ordinary chemically pure acid, the solution turns yellow on standing and red by warming. The red is easily obtained by dissolving in a little dilute acid, then evaporating from a test-tube very slowly by means of a small flame. After the red liquid cools a trace of nitric acid changes it to violet.

378. Concentrated nitric acid dissolves narcotin to a yellow solution.

379. Fröhde's reagent of the ordinary strength dissolves narcotin, forming a green solution. If stronger (0.01 gm. molybdate in 1 c.c. of acid) the green solution soon changes to a cherry-red.

380. Erdmann's reagent gives a red solution.

381. Vanadium sulphate gives a red color likewise.

Strychnin, $C_{21}H_{22}N_2O_2$

Strychnin is soluble with difficulty in water, its salts much more easily so. It is one of the most intensely bitter of the

alkaloids. It gives reactions in very dilute solutions with most of the general alkaloidal reagents. The chlorids of gold and platinum do not react in very dilute solutions, perhaps below 0.1 per cent. to 0.01 per cent.

382. Strychnin forms a colorless solution with concentrated sulphuric acid.

383. To the dry substance add a drop of concentrated acid, about one part water to five parts of acid, then by means of a glass rod, draw through the solution a minute crystal of potassium dichromate. A series of colors results, always in the same order; first blue which quickly becomes violet, then more slowly red, pink, and yellow. The colors are characteristic of strychnin and, when the substance is pure will be produced by as small an amount as the fifty-thousandth of a grain. The reaction is, however, interfered with by the presence of a number of organic compounds, including morphin.

384. Vanadium sulphate in concentrated sulphuric acid dissolves the solid compounds with the production, first of a blue, followed by a violet and red color. If it is then diluted with water the pink remains for a long time.

385. Cerium oxid with strychnin in concentrated sulphuric acid gives the same colors as the last reagent. It is said to react with the millionth of a gramme. To make the reagent heat cerium oxalate to redness to form the oxid and dissolve this in thirty times its weight of concentrated sulphuric acid.

386. Strychnin gives no color when treated with concentrated sulphuric acid and a molybdate, nitrate, or nitric acid.

387. Concentrated nitric acid colors strychnin or its salts only faintly yellow, if at all, when it dissolves them, but on standing the solution becomes a darker yellow (difference from brucin).



The alkaloid and most of its salts are crystalline.

388. Concentrated nitric acid dissolves brucin to a deep red

liquid, which on standing or heating becomes yellow. After this has occurred dilute the solution and with this a reducing agent, like stannous chlorid, will give a violet. An excess of nitric acid must be avoided or the reaction loses in sensitiveness. The violet solution when made alkaline with sodium hydroxid changes to blue or green. These changes are peculiar to brucin.

389. Concentrated sulphuric acid dissolves brucin without producing a color.

390. Chlorin water forms a bright red solution, the color being destroyed by an excess of the reagent and turned brownish-yellow by ammonium hydroxid.

Atropin (Daturin), $C_{17}H_{23}NO_3$

391. Atropin imparts a color to neither concentrated nitric nor sulphuric acid in the cold, but dissolves to a clear solution.

392. A crystal of atropin when moistened with three or four drops of fuming nitric acid leaves a yellowish residue when evaporated to dryness on a steam-bath. Let a drop of a solution of potassium hydroxid in 90-per-cent. alcohol run over the residue. Where they come in contact a reddish-violet color is produced.

393. If a milligramme of atropin is heated in a dry test-tube until vapors begin to appear and then 1 c.c. of concentrated sulphuric acid is added and the heating continued, the odor of flowers is observed. By cautiously diluting with 2 c.c. of water and warming further it may be made more distinct. On addition of small crystals of potassium dichromate to the concentrated acid solution the odor changes to that of oil of bitter almonds.

394. Platinic chlorid does not precipitate atropin or its salts (difference from most alkaloids).

395. A very dilute aqueous solution of atropin (1 : 100,000)

when applied to the eye causes a dilation of the pupil which lasts for a long time.

Veratrin

396. Veratrin dissolves in concentrated sulphuric acid which is free from nitrogen compounds to a colorless solution. On warming it changes to a crimson-red. In the ordinary chemically pure acid it makes a yellow solution, changing to orange, then blood-red and in half an hour, to a carmine-red. The addition of a minute quantity of nitric acid hastens these changes.

397. When warmed a few minutes in a small test-tube with 1 c.c. of concentrated hydrochloric acid the latter is colored a reddish-violet. No other alkaloid gives this reaction.

398. If mixed with 6 times the amount of cane-sugar, then moistened with concentrated sulphuric acid (only a little being added from a glass rod, not enough to make a solution) veratrin gives a dark green color, becoming purple and then blue in a few times. From the action of the acid on the sugar it finally turns brown and black.

Cocain, $C_{17}H_{21}NO_4$

399. Solutions of the alkaloid or its salts in water cause numbness when applied to the tongue and dilation of the pupil when applied to the eye.

400. Concentrated sulphuric acid dissolves the cocain or its salts without discoloration. When warmed it turns brown, the hydrochlorid giving the odor of hydrochloric acid. The vapors produced by heating with the concentrated sulphuric acid deposit benzoic acid on the sides of the test-tube on cooling.

401. Concentrated nitric acid gives no color with cocain in the cold.

402. With 1-per-cent. solution of potassium permanganate cocain yields a precipitate of cocain permanganate. This

upon standing collects in radiating clusters of thin tabular crystals, a bright reddish-purple in color, very plainly to be seen with a low power of the microscope.

403. An aqueous solution of cocain acidulated with dilute sulphuric acid, to which enough potassium permanganate solution has been added to give a violet color does not lose this after standing half an hour at the ordinary temperature.

404. If a little cocain hydrochlorid is powdered with as much mercurous chlorid in a dry porcelain dish the mixture is white, but it becomes gray in presence of a little moisture, even by being breathed upon.

405. Cocain or its hydrochlorid when evaporated to dryness on the steam-bath, after the addition of 1 c.c. of concentrated nitric acid, leaves a colorless residue. With a few drops of alcoholic potassium hydroxid it develops the pleasing and permanent odor of benzoic ethyl ester.

406. Cocain hydrochlorid solution with a few drops of potassium dichromate gives a yellow precipitate which quickly disappears. On acidifying the solution then with hydrochloric acid an orange-yellow crystalline precipitate of cocain chromate appears which is soluble in excess of the acid.

Quinin, $C_{20}H_{24}N_2O_2$

407. Quinin or its salts give no color with Erdmann's reagent, Fröhde's reagent or with concentrated nitric acid (difference from morphin).

408. Solutions of quinin, as well as many salts of quinin, after acidifying with sulphuric acid, give a bluish fluorescence, perceptible in very dilute solutions and a characteristic reaction. Concentrated acid dissolves the dry alkaloid to a similar fluid, with no brown or black color.

If the solution in sulphuric acid is exactly neutralized with ammonia, one drop of hydrogen peroxid and one of copper

sulphate solution added, then boiled, an intensely red color appears, changing slowly to blue, and finally green.

409. Ten c.c. of a solution of a quinin salt in water with two drops of bromin water or chlorin water and enough ammonium hydroxid to render it alkaline gives an emerald-green color—a characteristic reaction.

410. If to an alcoholic solution of quinin sulphate there is added tincture of iodine, and the mixture is warmed, then allowed to stand and cool, there separates a precipitate consisting of clusters of crystals, dark green by transmitted light and with a metallic luster by reflected light. The compound is called herapathite, and is characteristic of quinin.

Questions for Further Study on Organic Compounds

What are organic substances and how distinct is the line between these and the inorganic? Are benzene and benzin easily combustible? Why? What is the nature of substances of which the vapors form explosive mixtures with air? What is the difference in arrangement of atoms in the molecules of the above compounds? Under what circumstances is iodoform decomposed by air or light? What oxidizing agents oxidize alcohol or its solutions? What is produced by the action of strong mineral acids upon alcohol? Why do many tinctures give precipitates when diluted with water? Are there any which do not? Why? What compounds, organic and inorganic, are soluble in alcohol? In what beverages is amyl alcohol found and under what name? What is the value of glycerin as a solvent? Will carbolic acid neutralize solutions of the alkalies? With what solids does crystallized phenol form a liquid mass on trituration? For what is formaldehyd most extensively used? How can it be most readily generated? Where does meconic acid occur and what is its importance? What drugs contain a large propor-

tion of tannic acid? Are the aqueous solutions of gallic and tannic acid permanent? What would be the effect of triturating them dry with strong oxidizing agents? Is tannic acid incompatible with solutions of any other metals except antimony? Can starch be changed into glucose by other means than by mineral acids? What is the relation of this to "liver starch"? Does grape-sugar occur elsewhere than in the grape? What are the best means of distinguishing the three kinds of sugar? What is the relation of the alkaloids to the ptomaines? Is there any similarity in their reactions? Which are the liquid alkaloids? With what solids does anti-pyrin give a liquid mass on trituration? What is the difference between an isonitril and the cyanid of an organic radical? What are the mercaptols? Trituration with what solids and salol gives a liquid mass?

PART II

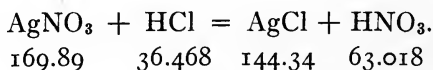
VOLUMETRIC ANALYSIS

CHAPTER I

GENERAL PRINCIPLES

In quantitative chemical analysis, that is, the determination of the amounts of the constituents of a compound or mixture, two methods may be employed, the gravimetric, where the constituent or some derivative of it is isolated and weighed, and the volumetric, where to a definite quantity of the substance there is added of a dissolved reagent just sufficient to complete some chemical change, such as precipitation, neutralization or oxidation. If the concentration of this reagent is known we can calculate from the volume necessary for the reaction the weight of the compounds acted upon.

For example, the concentration of a solution of silver which has been dissolved in nitric acid may be ascertained in two ways. We know that when the metal dissolves it forms silver nitrate, of which the formula is AgNO_3 . Of this the atom of silver weighs 107.88, of nitrogen 14.01, and the three atoms of oxygen 48.0, or a weight of 169.89 for the molecule. If hydrochloric acid is added to this solution silver chlorid is produced.



That is, one molecule of hydrochloric acid having a weight of 36.468 will convert 169.89 parts of silver nitrate into 144.34 parts of silver chlorid and 63.018 parts of nitric acid. The

silver chlorid, which forms a precipitate, can be filtered from the liquid, washed, dried, and weighed. Since of every 144.34 parts of the chlorid there are present 35.46 of chlorine and 107.88 of silver a simple proportion will give the weight of silver in the compound. Thus

$$144.34 : 107.88 = \text{weight of AgCl} : \text{weight of Ag.}$$

This is the gravimetric method.

In the volumetric method the hydrochloric acid would be made of such a concentration that each cubic centimeter would contain a known and definite weight of HCl. From the number of cubic centimeters of acid used and the concentration of each we can calculate the weight of HCl necessary to precipitate the silver. A proportion gives the weight of silver precipitated, this being equal to 107.88 parts of silver for each molecule of HCl. Thus

$$36.468 : 107.88 = \text{weight of HCl used} : \text{weight of Ag.}$$

Gravimetric methods require a considerable time for their completion and usually demand more manipulative skill than the volumetric. A very sensitive and somewhat expensive balance is also a necessity. On the other hand, the volumetric methods can be easily and rapidly carried out after the standard solutions are prepared and the apparatus is neither dear nor cumbersome. In some cases, on account of the impossibility of deciding when the proper amount of the reagent has been used, volumetric methods of analysis must be abandoned. However, since they are so convenient of application, they will be the principal ones studied here.

The measuring apparatus employed in volumetric chemical analysis is for the determination of volume and it is graduated according to the metric system (see table, page 242) because of the great readiness by which calculations can be made thereby. The unit most in use is the cubic centimeter (c.c.), with its divisions and multiples.

Measuring cylinders are narrow cylinders of glass with a foot. On account of the comparatively large surface of the liquid, whereby a slight variation in the height of the liquid makes a considerable difference in its volume they can only be used where accuracy is not essential. They will, however, roughly measure any volume less than their total capacity. Some are of the same diameter throughout their length and others are fitted with glass stoppers for convenience in shaking their contents.

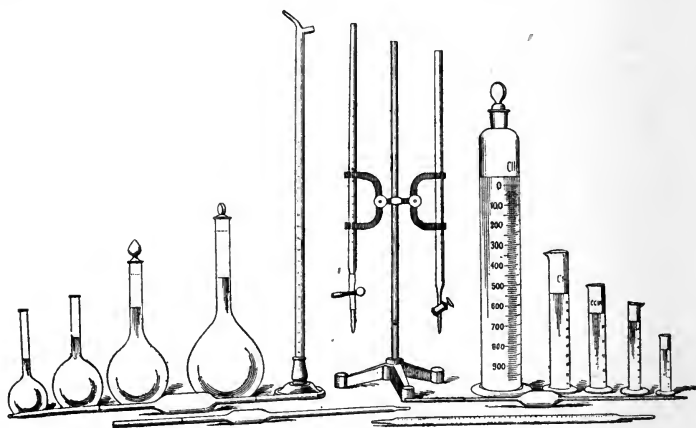


FIG. 13.—*Apparatus for Measuring.* 1. Flasks. 2. A pouring burette (Bink's form). 3. Two dropping burettes (Mohr's form) in a holder, one with a rubber tube and spring clamp, the other with a glass stop-cock. 4. Graduated cylinders. 5. In front are three pipettes with bulbs and one of the cylindrical form.

If accurate measurements of comparatively large volumes are necessary flasks serve the purpose better. Accuracy is gained by a narrow neck where they are marked to indicate the height to which they should be filled. It is advantageous to have two marks, the lower one of which shows where the liquid should stand when the flask contains the volume which it is designed to hold, for example, a liter, and the upper (but little above the first) to which the fluid must rise if the flask

is expected to deliver a liter when it is emptied. That is, allowance is made for the few drops which adhere to the inside of the vessel. Measurements can by this means be made of only one volume and no fractional parts of it. Measuring flasks are used for the preparation of the standard solutions that are employed in volumetric analysis. As variations in temperature cause expansion and contraction in the liquids the volume will be correctly measured only at that temperature at which the flask was calibrated. This is usually at 15° C.

A pipette is a measure used to deliver a definite and fixed volume also. It is made of a glass tube, either with an expansion or bulb in the middle or of the cylindrical form. To fill it the point is inserted in the liquid, then the air above is exhausted by the mouth until the liquid rises above the upper mark, when the tube is removed from the mouth and the top quickly covered with the forefinger. By slightly turning the finger the liquid, which should now stand above the mark, is allowed to flow out until the surface coincides with the mark. The pipette is then held over another vessel and the liquid is poured into this. Some pipettes have two graduation marks, one above the bulb and the other below. In this case the liquid must be allowed to escape only until it reaches the level of the lower one. If there is but a single graduation above the bulb, it should be emptied, and the last drop removed by touching the side of the vessel below. Pipettes of this shape are very accurate since the area of the tube is small as compared with that of the bulb. Each one will deliver only the volume for which it is calibrated. They are ordinarily not used for measuring over 100 c.c. The cylindrical form allows the measurement of fractions of its whole volume, being graduated throughout the greater part of its length. With the smaller sizes a rubber bulb or nipple slipped over the upper end enables the operator to regulate the flow to dropping or any desirable speed.

When measurements are to be made of varying volumes of liquid a burette should be employed. This is made of a cylindrical tube, carefully graduated into cubic centimeters and their fractions. It differs from the cylindrical pipette in not having its delivery regulated by the finger on the upper end. There are two varieties, the dropping and the pouring burettes. The flow from the former is usually regulated by a valve or stop-cock below. One with a glass stop-cock, although the most expensive, is preferable since rubber affects the strength of some solutions if allowed to remain in contact with them. (A little vaselin will prevent the stop-cock sticking.) Instead of this in many cases a short piece of rubber tubing can be slipped over the end of the burette and the amount of liquid delivered can be controlled by the compression of this by a spring clamp or pinch-cock. A solid bead of glass slightly larger than the inside diameter will also close the tube when placed within. By squeezing this between the thumb and forefinger the rubber is stretched and the contents of the burette slowly drops from the narrow jet below. Where frequent determinations are made with the same solution the lower part of the burette can be connected with the stock bottle of the same, thus permitting it to be filled without pouring into the top of the tube.

The pouring burettes vary somewhat in form, but are essentially a long, narrow tube graduated like the others but closed at the bottom. From these the solution is poured out of a small jet at the top, and the amount thus used is indicated by the difference between the height of the liquid before and after the pouring. By holding the finger over the large tube to govern the admission of air the flow can be exactly regulated. They have no rubber parts to change the strength of the solutions used in them and do not cost as much as those with glass stop-cocks.

An examination of the surface of a liquid in a glass vessel,

particularly if this is a narrow one, shows that the surface is not flat but concave or saucer-shaped. This is called the meniscus. It results from the attraction between the glass and liquid which causes a rising of the latter at the circum-

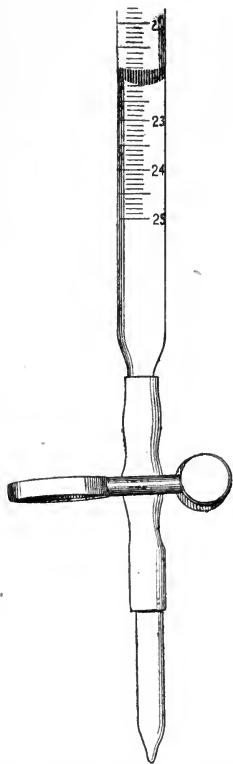


FIG. 14.—The lower part of a Mohr's burette with spring clamp, showing the meniscus.

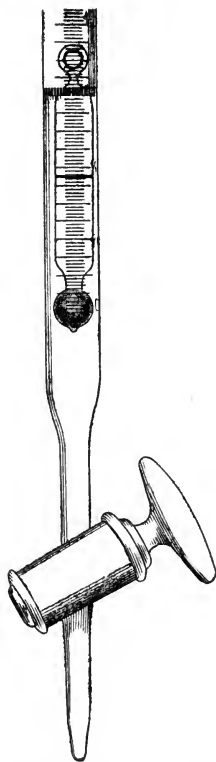


FIG. 15.—The lower part of a Mohr's burette with glass stop-cock and Erdmann's float in the solution.

ference. When seen from the side it is sometimes a matter of uncertainty which part should be regarded as the top of the column. In measuring with a burette it is a matter of indifference providing the same part is always used. With deeply

colored liquids only the upper line can be distinguished. With colorless ones the lower margin of the meniscus is most distinct, especially if a white card is held behind it. In all cases the eye of the observer must be on the same level as the meniscus. The Erdmann's float or swimmer may be employed as an aid in determining how much the column has fallen in the burette. This is a narrow tube weighted so as to float vertically in the burette. A line around the float is the measuring point instead of the meniscus.

The standard solutions employed in volumetric analysis are of two kinds, the normal and the empirical. A normal solution $\left(\frac{N}{1}\right)$ contains in one liter a number of grammes of the reagent equal to its molecular weight, provided the molecular weight of the reagent is equivalent to one atom of hydrogen. Otherwise one liter contains such a fraction of the molecular weight as is the equivalent of one hydrogen atom. For example,

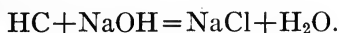
Reagent.	Active Component.	Valence of Active Component.	Molecular Weight.	Normal Solution Grammes per Liter. ¹
HCl	H'	I	36.468	36.468
NaOH	OH'	I	40.008	40.008
NH ₄ OH	OH'	I	35.05	35.05
Na ₂ CO ₃	CO ₃ ''	II	106.0	53.0
H ₂ SO ₄	H ₂ ..	II	98.086	49.043
H ₂ C ₂ O ₄ , 2H ₂ O	H ₂ ..	II	126.048	63.024
H ₃ PO ₄	H ₃ ..	III	98.024	32.675
2KMnO ₄	O ₅ ²	V	158.03	31.606

Since there are 1,000 c.c. in a liter, each cubic centimeter of a normal solution contains as many milligrammes of the reagent as there are grammes in the liter. One cubic centimeter of a normal solution is the equivalent of one cubic centi-

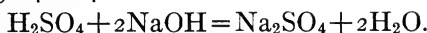
¹ In making normal solutions, unless exceptional accuracy is required, the weighings do not need be carried farther than two decimal places.

² KMnO₄ acts as an oxidizing agent, two molecules yielding 5 atoms of oxygen.

meter of any other normal solution. This is illustrated by the following examples.

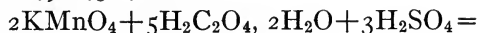


$$36.468 \quad 40.008$$



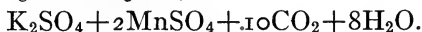
$$2)98.086 \quad 80.016$$

$$49.043 \quad 40.008$$



$$10)316.06 \quad 630.24$$

$$31.606 \quad 63.024$$



The equations represent the chemical actions taking place between different compounds, the numbers below giving the weight of the one or more molecules which enter into the reaction. In all cases these weights are seen to be in the same relation as those in the cubic centimeter of the normal solution, therefore equal volumes of such normal solutions are equivalent in their power.

In many determinations a normal solution is too concentrated for use and one of a fractional amount may be substituted. One-tenth of the normal (decinormal, $\frac{N}{10}$) or one one-hundredth of the normal (centinormal, $\frac{N}{100}$) are common. These are prepared by placing in a measuring flask one-tenth or one one-hundredth of its volume of the normal solution, then diluting to the mark. In the same manner others can be made if more convenient.

An empirical standard solution is not made up in the same manner as the normal, but is represented by Fehling's solution for the determination of glucose and some other sugars. Enough copper sulphate is taken so that 1 c.c. will oxidize 0.005 grm. of glucose.

The operation of volumetric analysis is called titration, and the analyst speaks of titrating the substance under investigation. The process is to place the standard solution in a burette, noticing the exact height of the liquid if it does not stand at the zero mark. From this the solution is allowed to flow slowly into the liquid that is being tested, stirring continually to cause immediate mixing. When enough of the reagent has been added to complete the reaction the amount is carefully read from the burette and the unknown quantity of the other substance is calculated. In order that a volumetric method of quantitative analysis should be exact it is necessary that the end reaction, or point when sufficient of the reagent is present, should be plainly visible through some change in the appearance. Sometimes this occurs spontaneously when the chemical change is complete, but very often a third substance called an indicator must be added.

The calculation of the results may be made in a number of ways. It should be remembered that although the measurements are by volume the results are in terms of weight and that therefore volume should be converted into weight as soon as possible. Suppose that in the determination of the percentage of silver in an alloy with copper after dissolving one gramme of the alloy in nitric acid 5.0 c.c. of the normal hydrochloric acid should be exactly sufficient to precipitate the silver. Each c.c. of the normal solution containing 0.036468 gm. of HCl, 0.18234 gm. of HCl would have been thus used. By the method of proportion given on page 149 we have

Molecular Weight of HCl : Atomic Weight of Ag =

$$36.468 \quad : \quad 107.88 \quad =$$

Weight of HCl : Weight of Ag

$$0.18234 \text{ gm.} : 0.5393 \text{ gm.}$$

or 53.93 per cent. of silver in the alloy.

Or again, as the equation on page 149 shows that each cubic centimeter of normal HCl precipitates 0.10788 gm. Ag, the

amount of silver present can be obtained by multiplying this by the volume of the acid used. That is (since normal solutions contain $\frac{\text{molecular weight}}{1000}$ of univalent compounds, $\frac{\text{molecular weight}}{2000}$ of bivalent compounds, etc., and since one cubic centimeter of this normal solution acts upon $\frac{\text{molecular weight}}{1000}$ of other univalent compounds, $\frac{\text{molecular weight}}{2000}$ of other bivalent compounds, $\frac{\text{molecular weight}}{3000}$ of other trivalent compounds, etc.) in volumetric determinations *multiplication of the number of cubic centimeters of a normal solution necessary for a complete chemical reaction, by $\frac{\text{molecular weight}}{1000}$ of a univalent compound, whose amount is being ascertained or by $\frac{\text{molecular weight}}{2000}$ of bivalent compounds, etc., gives the weight of the latter in grammes.*

CHAPTER II

ANALYSIS BY NEUTRALIZATION

OF this there are two kinds, acidimetry—the determination of acids, or substances with an acid reaction—and alkalimetry—the determination of alkalies, or substances having an alkaline reaction. A standard alkali or acid is added from the burette to the solution of unknown strength until the reaction of the mixed solutions is neutral. The point is shown by the addition of an indicator. This is a substance which is of one color in liquids of alkaline reaction and another when the reaction is acid. A number of such are used in acidimetry and alkalimetry. In some instances one is to be preferred and in some another, so that there can be no such thing as the best indicator for all cases. Some from their color, cannot be used with liquids of a certain shade; some have their sensitiveness lessened, or their action prevented, by ammonia, carbon dioxid, etc.; some are affected by mineral acids, but not by organic acids, so that the selection of the proper indicator is a matter of importance. The properties of some of the most common are given in Table VII.

The Preparation and Properties of Standard Solutions

These can be prepared either by standardizing by means of other standard solutions, when it is inconvenient or impossible to weigh the reagent which is to be dissolved, as in the case of gaseous reagents or those which contain an indefinite quantity of water. Or they may be made, as is most frequent, by weighing out the proper amount of the solid

TABLE VII
INDICATORS FOR ACIDIMETRY AND ALKALIMETRY

Name.	Color in Acid Solutions.	Color in Alkaline Solutions.	Advantages.	Objections and Interferences.	Remarks.
Litmus.	Red.	Blue.	Seen with sodium flame red appears colorless; blue becomes very dark.	CO ₂ prevents sharp end-reaction; cannot well be used for carbonates. Unsatisfactory with phosphoric and many organic acids.	If used with carbonates the CO ₂ must be expelled by boiling
Phenolphthalein.	Colorless.	Reddish-pink	Very sensitive, changing suddenly with reaction. Can be used with alcoholic solutions, also with many colored liquids. It is affected by both mineral and organic acids.	Inadvisable with carbonates (CO ₂) or ammonia compounds. Useless with borax.	CO ₂ can be expelled by boiling. With phosphoric acid it indicates neutrality when two hydrogen atoms are replaced by a metal.
Methyl orange.	Pink.	Faint yellow.	Can be used with carbonates, sulphides and borates, also ammonium compounds.	Cannot be used with most organic acids. Change of color is indistinct by artificial yellow light.	With phosphoric acid indicates neutrality when one hydrogen atom is replaced by a metal. Only a few drops should be used.
Rosolic acid also called aurin and corallin.	Pale yellow.	Violet-red.	Can be used with mineral acids and oxalic acid.	Is not reliable for other organic acids. Its sensibility is lessened by CO ₂ or ammonium compounds.	
Cochineal.	Reddish-yellow.	Violet.	Can be used with ammonia and by gas light. CO ₂ does not interfere. The change of color is well marked with the alkaline earths.	Traces of iron, aluminum compounds or acetates interfere.	
Lacmoid	Red.	Blue.	Can be used for mineral acids alone or in presence of metallic salts, also with borates.	CO ₂ interferes; cannot be used with carbonates except while boiling.	Many metallic salts like sulphates and chlorides of iron, zinc and copper are neutral to lacmoid though acid to litmus

reagent, placing this in a measuring flask (usually one holding a liter) filling it to the mark with distilled water of a temperature of 15° and thoroughly mixing after solution has occurred. When not in use they should be preserved in tightly closed bottles. Some slowly change for a long time after they have been prepared, and others are so unstable that special methods of preservation must be employed and their concentration must be determined before each new series of analyses. Too great pains cannot be taken to insure correctness in the standard solutions.

Standard Solutions for Acidimetry and Alkalimetry

Normal Sodium Carbonate, Na_2CO_3 .—Pure anhydrous sodium carbonate is to be heated to a low red heat and after cooling, 53.00 grms. is dissolved in pure water and the volume made up to one liter. If the pure salt is not at hand 85 grammes of sodium bicarbonate, which is usually easily obtained in the pure state, will, by heating to drive off the water and carbon dioxid, give rather more than this weight of the pure carbonate.

Normal Sodium Hydroxid, NaOH .—This contains in one liter 40.008 grammes of pure NaOH . Since the solid substance as purchased contains a varying amount of moisture and consequently cannot be accurately weighed, the solution should be made at first stronger than is required, its strength ascertained, and should then be diluted with the calculated volume of water. As both the solid and the solution unite with carbon dioxid care must be taken to prevent its access to them. Put about 45 grammes of pure, dry sodium hydroxid into a liter flask and fill to the mark with cold distilled water from which the carbon dioxid has been lately expelled by boiling. After dissolving and thorough mixing remove 10 c.c. by a pipette to a beaker and add a few drops of phenolphthalein solution. From a burette run in normal

hydrochloric acid until, after stirring, the pink color has been just destroyed. Repeat this several times and if the determinations nearly agree take their average; calculate the concentration of the alkaline solution and the amount by which it must be diluted to make it normal. If, for example, 11 c.c. of the normal acid is necessary to neutralize 10 c.c. of the sodium hydroxid, where if the latter were normal only 10 c.c. of acid would be required, the alkali is more concentrated than normal. Enough water must be added to dilute each 10 c.c. of the hydroxid to 11 c.c.—that is, the one-tenth of its bulk. For example, if 50 c.c. of the liter first prepared have been used in the preliminary testing, 95 c.c. of water should be added to the remainder (in a larger flask, since this makes more than a liter). If the determination was correct 10 c.c. of this solution will now exactly neutralize 10 c.c. of the normal acid. For preservation the solution should be kept in a bottle having a two-holed rubber stopper. Through one hole passes a syphon tube with a rubber tube and spring clamp on the end; to the other is attached a U-tube filled with small fragments of soda-lime. The air can pass through this, but its carbon dioxide is absorbed. Other standard alkaline solutions, ammonium, potassium or barium hydroxide, etc., can be prepared in a similar manner.

Normal hydrochloric acid, HCl, contains 36.468 grm. in a liter. Since the acid as purchased is of variable concen-

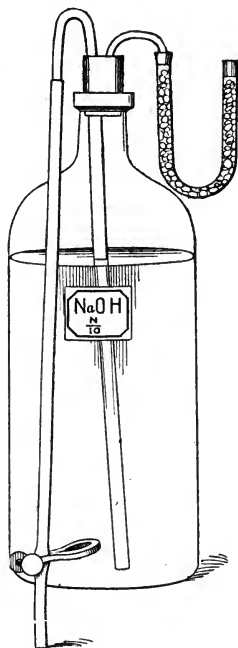


FIG. 16.—Bottle for the preservation of standard solutions which are affected by the carbon dioxide of the air.

tration, the normal acid must be made by standardizing by means of a standard alkaline solution. Dilute about 130 c.c. of the concentrated hydrochloric acid (specific gravity 1.16) to a liter, which will make it above normal concentration. Mix well and remove 10 c.c. to a small beaker, adding a few drops of methyl-orange solution. From a burette allow a normal sodium carbonate solution to flow slowly in, stirring meanwhile, until the color of the liquid changes from a pink to a pale yellow. Take the average of several determinations and calculate the amount by which it must be diluted to make 10 c.c. of one solution neutralize 10 c.c. of the other. Add this and test it to make sure that it is correct. Thus if 10 c.c. of the acid requires 12.5 c.c. of the normal carbonate to neutralize it, for each 10 c.c. of the acid 2.5 c.c. of water must be added.

Normal oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, contains 63.024 grms. of the crystallized solid per liter. The solution may be prepared by weighing out this amount if the crystals are bright in appearance and free from moisture. They are, however, very efflorescent, losing a great part of their water of crystallization when exposed to the air, then becoming dull in appearance, and should not be used for making the solution by weight. The pure crystals leave no residue if they are ignited on platinum foil. If such a residue remains it is a sign of an impurity. If the pure crystals cannot be obtained a slightly greater weight than given above may be taken (perhaps 65 grammes), and, after dissolving in water in a liter flask and diluting to a liter, the concentration may be learned by titrating with the normal sodium hydroxid, using phenolphthalein for the indicator. This solution will be too concentrated and should be reduced by adding the calculated amount of water as in the preparation of normal hydrochloric acid. The solution decomposes in direct sunlight. Very dilute solutions do the same in weak light so that if decinormal or centinormal solutions are needed the normal solution should only be diluted with water shortly before it is to be made use of.

Other acids, sulphuric, tartaric, etc., can be standardized by a similar course of procedure.

Acidimetry

For the standard solution normal sodium carbonate or sodium hydroxid may be used. Place this in the burette, making a note of its height if it is not at the zero mark, and with a pipette carefully measure a definite volume, perhaps 10 c.c. of the liquid of which the acidity is to be determined, transferring it to a small beaker. To this add a few drops of the indicator, selected in accordance with Table VII. For the titration let the standard alkali flow slowly into the acid, stirring meanwhile in order to thoroughly mix the two liquids. At first the color, produced when the alkali meets the indicator, vanishes immediately. When it disappears only slowly the normal solution should be added by drops so as to avoid an excess, stopping when the change in color of the indicator is persistent throughout the liquid. The amount drawn from the burette should be ascertained and noted and the titration repeated. It is best to take the average of several nearly concordant results than to depend upon one. Knowing the weight of each acid which will be neutralized by one cubic centimeter, the weight present in the volume used can be calculated. The final results can be expressed as grammes per liter or in percentage by weight. In a liter of water there are 1,000 grammes (c.c.) and consequently if the liquid being tested is of the same specific gravity as water the percentage by weight (that is, parts in a hundred) can be obtained from the grammes per liter by dividing by ten. When the specific gravity is greater or less than one the result so obtained must be divided by the specific gravity to find percentage. It is to be understood, of course, that acids combined in neutral salts cannot be determined in this manner.

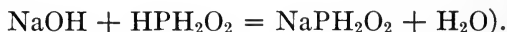
Practical Exercises in Acidimetry

1. Determine the concentration of dilute sulphuric and nitric acids furnished by the instructors, reporting results. Use normal sodium carbonate, with methyl orange for an indicator.¹

2. From concentrated hydrochloric acid prepare a normal solution according to the directions on page 161.

3. After the preparation of normal sodium hydroxid (page 160) standardize a normal solution of oxalic acid (page 162).

Other chemical compounds which have an acid reaction can be determined quantitatively by similar methods after the choice of a suitable indicator. Among those with which sodium hydroxid and phenolphthalein can be used are acetic acid (vinegar), lactic acid (sour milk) or acidity of gastric contents (with $\frac{N}{10}$ NaOH), aromatic sulphuric acid, hydrobromic acid, hypophosphorous acid, HPH_2O_2 (univalent, the equation being



In all cases the basicity of the acid—that is, the number of hydrogen atoms which can be ionized, must be considered, as this determines the amount of alkali necessary to neutralize the molecule.

Alkalimetry

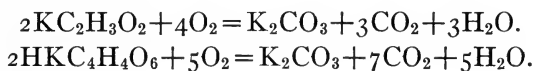
In this the operations of acidimetry are reversed, the standard acid solution being placed in the burette and the alkaline solution below. Otherwise the method is as before. In addition to its use in determining the amount present of a substance with an alkaline reaction it can be used for the same purpose with another class of compounds—that is, the salts of

¹ In the practical exercises a single titration ought not to be depended upon but the average of two or three closely agreeing ones should be taken.

organic acids which have as a base one of the alkali metals. These when ignited are changed into carbonates of those metals. The carbonates are alkaline in reaction although the salts from which they are derived may be acid or neutral. One molecule of the carbonate requires for its formation a sufficient number of molecules of the organic compound to furnish two atoms of a monovalent metal. Thus one molecule of a normal tartrate gives one molecule of carbonate,



Two molecules of an acetate or acid tartrate form the same amount.



Two molecules of a normal citrate form three of a carbonate.



It will not be necessary to burn off all the carbon to form the carbonate—that is, to heat long enough to leave a perfectly white residue. If the organic salt is at first in solution a measured amount must be evaporated to dryness, then the solid must be heated in a platinum or porcelain crucible, gently at first, to avoid loss, then until the mass is completely carbonized, which will require a red heat. If the compound is a solid, a weighed quantity (one to two grammes) should be treated in the same way. After cooling the carbonate will dissolve easily in hot water. It should be filtered and the carbon washed with small amounts of hot water until it is no longer alkaline. The weight of carbonate can be determined by titration and, knowing the number of molecules of the organic salt from which one of the carbonate is derived together with their relative molecular weights, the weight of the original salt is readily calculated.

Practical Exercises in Alkalimetry

1. Using normal hydrochloric acid for the standard, determine the concentration of an unknown solution of ammonium hydroxid with cochineal or rosolic acid as indicator; of borax with lacmoid as an indicator.

2. Prepare a normal solution of ammonium hydroxid by the method outlined on page 161.

3. Ignite thoroughly in a platinum or porcelain capsule a weighed amount of acid potassium tartrate, extract with hot water, titrate the filtrate, using normal hydrochloric acid and methyl orange, and from calculated result form an opinion as to the purity of the tartrate.

4. Evaporate to dryness in a porcelain capsule 10 c.c. of a concentrated solution of sodium acetate, ignite, titrate the soluble part and calculate the concentration of the solution.

Among the other compounds of which the amounts can be found by alkalimetry are the hydroxids and carbonates of the alkali metals, the hydroxids of the alkaline earths, the tartrates of sodium and potassium, the acetate of potassium, the citrates of potassium and lithium, the benzoates of lithium and sodium, the salicylates of lithium and sodium.

CHAPTER III

ANALYSIS BY OXIDATION (OR OXIDIMETRY), AND BY
REDUCTION

THE method is based upon the fact that certain compounds have the power of oxidizing definite amounts of other compounds when in solution. In some cases the end of the reaction is indicated by a change in the color of the standard; in others indicators are added. The results obtained are very accurate. The most common oxidizing agents used for the standard solutions are potassium permanganate, KMnO_4 ; potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, and iodine.

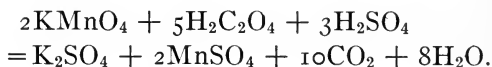
The Preparation and Properties of Standard Oxidizing Solutions

Potassium permanganate, KMnO_4 , can be obtained pure in the crystalline form, though it is so often impure that the solution should be tested after making by titrating against a standard. The crystals dissolve to an intensely reddish-purple solution. The molecular weight of the substance is 158.03. As stated before (page 154) when it acts as an oxidizing agent two molecules yield five atoms of oxygen. The combined valences of the five atoms of oxygen given by this double molecule is ten. Therefore a normal solution would contain one-tenth the double molecular weight of the salt in a liter or 31.606 grammes. The decinormal solution containing 31.606 is more commonly employed. This solution is likely to undergo slight decomposition on standing, although it will maintain its strength for several weeks. Unless freshly prepared it should be standardized before the solution is used, in the same manner as in the

original preparation. Organic matter produces changes in the solution, which should therefore not be brought into contact with rubber. A pouring burette or one with a glass stop-cock is suitable for its measurement. When the permanganate gives up its oxygen, providing a free mineral acid is present, the purple color disappears as a result of the formation of the colorless manganese salt of the acid. That is, the manganese, which was a part of the anion, becomes the cation. This decolorization indicates the completion of the reaction. An indicator is therefore unnecessary. If the crystals are known to be pure the weighed amount can be dissolved in a liter of water. In case of doubt as to their purity about 3.5 grammes should be so dissolved, the concentration of the solution ascertained by one of the following methods and the proper volume of water added to reduce it to the desired concentration.

The substances most commonly used to ascertain the concentration of a permanganate solution are oxalic acid, ammonium ferrous sulphate, and metallic iron.

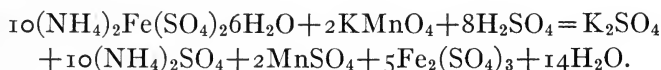
A decinormal solution of oxalic acid can be taken as the standard. The reaction is



The 10 c.c. of the oxalic acid is measured with a pipette and after acidifying with dilute sulphuric acid, is placed in a flask or beaker and the mixture warmed to about 60°. Then the permanganate solution is allowed to run in. At first the color disappears slowly but afterward more rapidly. If it turns brown the amount of sulphuric acid is insufficient. The permanganate should be added cautiously to avoid an excess, stopping when the pink color is permanent. From the average of several determinations calculate the concentration of the permanganate solution, remembering that if it were decinormal exactly 10 c.c. would be reduced by the oxalic acid.

Find the volume of water which will, if added, produce the decinormal solution, as in the preparation of standard solutions of sodium hydroxid (page 160) or hydrochloric acid (page 161). After dilution test again to see if the result is correct. It is well in this second test to make use of another standard solution such as one of decinormal ferrous ammonium sulphate.

Ferrous ammonium sulphate, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, can be obtained pure in the form of greenish crystals. For this purpose they must not have lost any of their water by efflorescence or be at all brown in color, which indicates that the iron is changing to the ferric form. A decinormal solution containing 38.41 grams to the liter should be used with sulphuric acid in the same manner as in the titration by oxalic acid. The reaction is



Here as before one cubic centimeter of the iron solution should decolorize exactly one of the decinormal potassium permanganate.

If metallic iron is the standard about 0.1 gm. of the purest piano wire, accurately weighed, should be dissolved in a flask by means of dilute sulphuric acid. Access of air can be prevented by a Bunsen valve made of a short piece of slit rubber tubing slipped over the exit tube and closed at the upper end, which allows the hydrogen to escape (Fig. 17). When the wire has dissolved, the solution can be diluted with recently boiled water and immediately titrated with the permanganate. The reaction is similar to that with the ammonium ferrous sulphate because the iron in dissolving forms ferrous sulphate, FeSO_4 . Since all iron contains carbon, allowance must be made for this. If it has not been determined in the sample which was used, the wire may be estimated at 99.6 per cent. pure.

Of *iodin* the decinormal solution is used. This contains 12.692 grms. in the liter. It can be made by dissolving about 18 grms. of pure potassium iodid in 200–300 c.c. of water in a

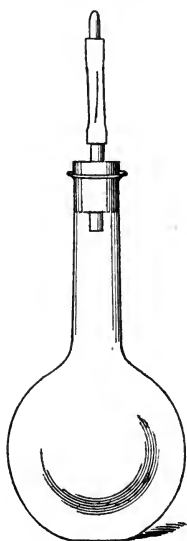
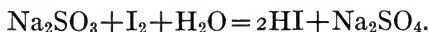


FIG. 17.—Flask fitted with Bunsen valve which allows the gas to escape from within but prevents the access of air.

liter flask, adding 12.692 grms. of chemically pure iodine and when this has dissolved, filling to the mark with water. If pure iodine cannot be obtained somewhat more than this weight may be dissolved and the concentration of the solution be ascertained by titrating with a standard solution of sodium thiosulphate (hypo-sulphite) in the manner described below. The iodine solution should be kept in a cool, dark place, but even then it does not maintain its concentration, so that unless it has been recently prepared it should be standardized before using.

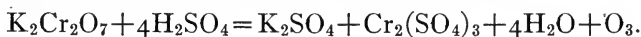
The oxidizing action of the iodine is an indirect one. It unites with the hydrogen of the water present, leaving the oxygen free to combine with oxidizable substances. This is illustrated by its action on sodium sulphite or arsenous oxide.



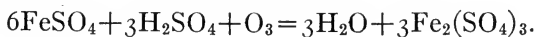
Although solutions of free iodine have a color and most solutions of its compounds do not, the distinction is not great enough to accurately mark the end reaction. Therefore a few drops of a boiled starch solution are added as an indicator. This gives a deep blue color as long as any free iodine is present and is colorless when the iodine is in combination with other elements.

Decinormal potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, which is often

used in oxidimetry, contains 4.907 grms. in a liter. The crystallized salt can be obtained in a pure state and the solution may be made by drying the salt at 100° , then dissolving this weight in water and diluting to a liter. The solution is much more permanent than that of potassium permanganate or iodine and is not affected by contact with rubber. An indicator must be used with it in the volumetric tests of ferrous compounds and this lessens its convenience. When the dichromate is used as an oxidizing agent it loses three atoms of oxygen. It is for this reason that its decinormal solution contains one-sixtieth of its molecular weight in grammes per liter (page 154). The sulphuric acid combines with the potassium and chromium forming the sulphates of these metals. Thus



The principal use of the dichromate solution in volumetric analysis is in the quantitative determination of iron and its ferrous compounds. If a ferrous compound is present with an acid the oxygen unites with the hydrogen ion of the latter, and the anion combines with iron, changing it to the ferric state.



Analysis of Reduction

This is the opposite of oxidimetry. Soluble reducing agents, or deoxidizers will remove oxygen from many of its compounds when in solution and if the end of this reducing action is definitely marked they may often be employed in the preparation of standard volumetric solutions. Oxalic acid and sodium thiosulphate are very commonly used. The former has already been discussed.

Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, contains in a liter of the decinormal solution 24.822 grms. of the crystallized salt. The solution can be prepared by dissolving in water this

weight of the pure crystals which have been dried by pressing in blotting-paper after pulverizing, then diluting to a liter. The solution should be kept in the dark. It even then decomposes slowly, however, so that old solutions cannot be depended upon. Sodium thiosulphate is principally used in volumetric analysis in the determination of free iodine. This includes the determination of other substances like bromine and chlorine, one atom of either of which sets free one atom of iodine from an iodide. If, therefore, to a solution of free bromine or chlorine a little potassium iodide is added, the bromine or chlorine frees the iodine. The amount of iodine thus liberated indicates that of bromine or chlorine.

Practical Exercises in Analysis by Oxidation and Reduction

1. From the normal solution of oxalic acid previously prepared make a decinormal solution by diluting one volume with nine of water. By the aid of this standardize a decinormal solution of potassium permanganate by the method described on page 168.

2. With the decinormal permanganate makes a determination of the amount of iron in a solution of ferrous sulphate, calculating the weight of Fe and FeSO_4 present.

3. By the aid of a decinormal solution of potassium dichromate (made by the directions given) make a titration of the same ferrous solution. Determine the end of the reaction by removing a small drop of the solution on the end of a glass rod and with this stirring a drop of a dilute, freshly prepared solution of potassium ferricyanide as an indicator. As long as there remains any of the unoxidized iron a blue color will result. When sufficient dichromate is present only a brownish-yellow appears. The tests are most conveniently made by placing a number of drops of the indicator on a porcelain plate and touching these with the stirring rod after the addition of each portion of the dichromate. The results obtained

by this method should agree with those by the permanganate. They thus serve to confirm the correctness of the dichromate solution as well as of the accuracy of the determination of the amount of iron.

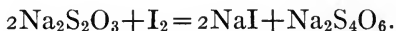
4. Use the decinormal permanganate to determine the concentration of a solution of hydrogen peroxid (dioxid). The reaction is $5\text{H}_2\text{O}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$. Measure into a beaker one cubic centimeter of the peroxid by means of a pipette and dilute with 10 to 20 times its volume of water acidified with H_2SO_4 . From a burette add the permanganate slowly until there is a permanent pink color. (In the U. S. P. process 10 c.c. of the peroxid are diluted to 100 c.c., and 16.9 c.c. of this is titrated. The Pharmacopœia requires it to decolorize 30 c.c. of the decinormal permanganate. This corresponds to a 3 per cent. solution by weight.) Calculate the percentage strength of the hydrogen peroxid solution by weight.

Instead of being expressed by weight the concentration of the hydrogen peroxid is often referred to the volume of oxygen which it will evolve when decomposed by heating. One atom is thus set free from each molecule, or one-half the amount that is given off when it is acted upon by potassium permanganate, as represented by the above equation. For each two molecules of the permanganate which are decolorized, therefore, there are present five atoms of active oxygen in the peroxid. Consequently 1 c.c. of the decinormal permanganate corresponds to 0.0008 gram. of such active oxygen. From the results obtained in the above determination of the concentration of hydrogen peroxid by weight calculate its oxygen volume of active oxygen, using 0.00143 gram. as the weight of one cubic centimeter of oxygen.

5. Iron is determined quantitatively by permanganate or dichromate solutions, but only when it is in the ferrous form. Hence ferric compounds must be reduced to ferrous before

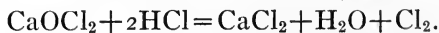
they are titrated. This can be effected by a number of reducing agents. Place in a flask fitted with a valve as described above (page 170) 10 c.c. of a ferric solution, acidify with sulphuric acid and add a few small fragments of granulated zinc which is free from iron or in which the amount of iron is known (using than a definite weight of zinc). Let it dissolve completely when, if the iron is reduced, the liquid will be colorless with no yellow tint. Then titrate immediately with the decinormal permanganate solution and, after the amount of iron has been found, calculate the weight and percentage of the ferric compound in the original solution.

6. With the aid of a decinormal solution of sodium thiosulphate determine the concentration of a solution of iodine, as follows: Into a measured volume of the iodine solution run, from a burette, the standard thiosulphate until the brown color has almost disappeared. Then add a few drops of a starch solution and continue the titration until the blue is just destroyed, leaving the liquid colorless. The reaction is then completed, the thiosulphate being converted into a sodium tetrathionate,



7. Chlorine or bromine when brought into contact with potassium iodide liberates an equal number of atoms. In consequence of this action the concentration of chlorine or bromine water is easily found. To 10 c.c. of the solution add about half a gramme of potassium iodide in crystals or solution and titrate with thiosulphate, using starch as an indicator, as in the last operation.

8. In the same manner determine the amount of available chlorine in calcium hypochlorite, CaOCl_2 .



Acidify a known quantity with hydrochloric acid after the

addition of potassium iodid and starch, and titrate with the thiosulphate as in the preceding exercises.

The presence of chlorates lessens the accuracy of the last determinations.

9. With starch as an indicator compare the concentration of the decinormal thiosulphate with the decinormal iodine solution to prove that both are correct.

10. When a ferric salt is warmed with potassium iodid it is changed to the ferrous state, one atom of iodine being set free for each atom of iron.



The quantitative method of determining ferric compounds based upon this reaction is carried out in the following manner:

To 10 c.c. of the ferric solution add about a gramme of potassium iodid and 2 c.c. of hydrochloric acid. By the above reaction the iodine is slowly set free. The mixture should be placed in a 100 c.c. glass-stoppered bottle and the whole warmed in water two hours at 40°. The temperature should not be allowed to exceed this nor the stopper be removed because of danger of loss of iodine through volatilization. Cool, and after the addition of a few drops of starch solution, titrate with decinormal sodium thiosulphate. Calculate the amount of the ferric salt, reckoning one atom of iron for each one of free iodine.

11. Prepare a decinormal solution of iodine by weighing (page 170), or take a larger amount than is necessary, dissolve in the same manner, determine its concentration by titration, and dilute to the standard.

12. With the standard iodine solution make a determination of a solution of arsenous acid, H_3AsO_3 , or an arsenite, like potassium arsenite, K_3AsO_3 . In the case of the arsenous acid pure sodium or potassium bicarbonate must be present to neutralize the hydriodic acid formed in the titration. Five to

ten times as much of this should be used as the estimated weight of the arsenous acid. The titration is carried out as before until the starch indicator is colored a faint blue. A gentle heat may be used to aid in the solution of the bicarbonate, but it cannot be heated high enough to decompose with bicarbonate as the carbonate thus produced would interfere with the action of the indicator. If a free alkali other than a bicarbonate is present it must be neutralized by hydrochloric acid and any acids must be neutralized with a bicarbonate before titration. The reaction between the iodine and arsenite is similar to that with the arsenous oxide already referred to.



CHAPTER IV

ANALYSIS BY PRECIPITATION

HERE the standard solution converts the compound of which the amount is sought, or some constituent of it, into an insoluble form, thus producing a precipitate. Knowing the amount of the standard necessary to effect this result the weight of the precipitate or of the substance from which it is derived can be calculated. As the point where precipitation is complete is, in almost all cases, indistinct, indicators are usually required in this class of analysis. These are such compounds as will not be acted upon by the standard until the compound under investigation has been completely transformed and which will then react with the excess of the standard solution producing a color or some other visible change.

Precipitation is also often used in combination with other methods of volumetric determination. Thus soluble compounds of barium, strontium, and calcium can be precipitated as neutral carbonates by ammonia and ammonium carbonate. If these precipitates are washed and suspended in water they can be titrated by solutions of the normal acids, their amount being calculated from the volume of acid necessary to produce an acid reaction. The equations representing the chemical change occurring during their solution may be represented by the following:



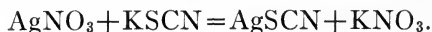
The Preparation and Properties of Standard Solutions Used in Analysis by Precipitation

Decinormal Silver Nitrate, AgNO_3 .—As the crystals can usually be obtained in the pure state, this can be made by dis-

solving 16,989 grms. in sufficient water to make the volume of the solution one liter. Or a somewhat greater weight may be dissolved, if the purity is doubtful, and the concentration ascertained by titration against decinormal sodium chlorid. Instead of the sodium chlorid decinormal hydrochloric acid can be used. In the latter case after the amount to be used has been accurately measured by a pipette, it must be carefully neutralized with sodium carbonate before the titration, avoiding an excess of the carbonate. The value of the silver nitrate in analysis by precipitation is that it forms insoluble compounds with the chlorids, bromids, iodids, and cyanids. The indicator is generally normal (yellow) potassium chromate. This forms an insoluble, dark red, silver chromate with the silver nitrate, but not until the above-mentioned compounds have been precipitated if they are present in the solution. The end reaction is most clearly seen if instead of daylight a yellow light, like that of illuminating gas, is used, the titration being conducted in a rather dark place.

The silver nitrate solution is decomposed by the action of light and by organic matter. It should therefore be preserved in an amber-colored bottle or in a dark place. It should be protected from dust and not be used in burettes which have rubber-tubing connections.

Decinormal Potassium Sulphocyanate, KSCN, contains in a liter 9.718 grms. of the salt. It cannot well be prepared by weighing the solid, since the latter is deliquescent. About 10 grammes of this should be dissolved in a liter of water and 10 c.c. of decinormal silver nitrate titrated with the solution after acidifying with 5 c.c. of dilute nitric acid. The reaction is shown by the following equation:



About ten drops of a solution of ammonium ferric sulphate (iron alum) is to be added for an indicator. The

silver sulphocyanate is precipitated first, giving the liquid a milky appearance. When all the silver has been converted into this compound the sulphocyanate acts on the indicator producing red ferric sulphocyanate which indicates the end reaction. With a solution prepared in this way less than 10 c.c. of the sulphocyanate should at first precipitate 10 c.c. of the decinormal silver nitrate. The amount of water which must be added to dilute it to correspond to the silver solution can be calculated as in the preparation of standard solutions of sodium hydroxid and hydrochloric acid. When this has been added it should be tested again in the same manner to ascertain its correctness. This sulphocyanate solution may be used for the estimation of silver, even in the presence of many other dissolved metals, since most of these are unaffected by the reagent. It can also be employed in connection with decinormal silver nitrate to determine the amount of any substance which is completely precipitated by the latter compound. This includes all those mentioned as capable of being determined by standard silver nitrate. In this case the method is that of *residual titration*. It consists in adding to the solution a measured quantity of the decinormal silver nitrate, greater than is sufficient to precipitate the compound, then titrating this with sulphocyanate to learn what the excess is. The difference in cubic centimeters between the volumes of silver nitrate used and sulphocyanate used shows the amount of standard silver solution which is taken up by the substance under investigation. From this its weight is obtained. The end reaction is rather easier to distinguish than when potassium chromate is the indicator.

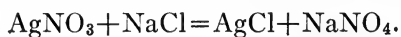
The standard solutions of silver nitrate and potassium sulphocyanate may be employed in the estimation of any compounds of the metals which can be converted easily and without loss into chlorids. This can be done with the carbonates, hydroxids, oxids and nitrates of potassium, sodium, ammo-

mium, calcium, strontium, barium, magnesium, and some other metals by the action of hydrochloric acid; also with the chlorates, which by ignition set free oxygen and are changed to chlorids. Carbonates may be decomposed with the evolution of carbon dioxid and nitrates with a setting free of nitric acid. This is accomplished by adding to a weighed or measured amount of the substance under investigation an excess of the acid (after evaporation to dryness in case of solutions) using concentrated acid with nitrates. The excess of the acid, that is, the part which has not united with the metal to form chlorids, must be completely driven off by first evaporating to dryness on a steam-bath, then heating in an air-bath at 120° until a piece of blue litmus-paper laid across the dish is no longer reddened. The chlorid is then dissolved in water and this solution titrated as before, using a known fraction of the liquid and making duplicate determinations. After the determination of the chlorin the weight of the metal, and hence of the original compound, can be calculated.

Practical Exercises in Analysis by Precipitation

1. Prepare decinormal silver nitrate by one of the methods given above.

2. With this solution determine the percentage concentration of a solution of sodium chlorid. Use only enough of the potassium chromate to make the solution slightly yellow, which will take but a few drops. With a large quantity it becomes more difficult to tell when the silver chromate commences to be permanent. Make the titration by yellow light or gas light if convenient (not that of an incandescent burner, however). One molecule of silver nitrate precipitates one of the chlorid.



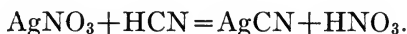
3. In the same manner determine the concentration of a solution of potassium bromid.

4. A potassium cyanid solution upon the addition of the silver ion forms at first no precipitate, but the soluble salt $\text{KAg}(\text{CN})_2$.



When all the potassium cyanid has been thus changed any excess of silver nitrate decomposes the double salt and a precipitate appears. This reaction can be made use of as a quantitative method. Into 10 c.c. of the potassium cyanid solution run from the burette decinormal silver nitrate, stirring continually. The equation above shows that as soon as a permanent precipitate appears, for each molecule of the silver nitrate used two of the cyanid have entered into reaction. One c.c. of decinormal silver nitrate accordingly corresponds here to 0.013 grm. of potassium cyanid, that is, twice as much as in corresponding reactions between other salts and silver nitrate, because of the formation of the double salt. In this method no indicator is necessary. Ascertain by it the percentage concentration of a solution of the cyanid.

5. With hydrocyanic acid silver nitrate gives the following reaction:



The nitric acid thus formed would interfere with the titration and must be neutralized. This can be done by stirring into the hydrocyanic acid that is to be titrated, after measuring, enough of an aqueous suspension of magnesia to give an alkaline, milky mixture. Then add a few drops of potassium chromate solution and the standard silver nitrate until the red silver chromate does not disappear after stirring. Avoid inhaling the vapor of hydrocyanic acid: It should not be drawn into the pipette with the mouth. It is better to weigh the original portion than to attempt to measure it.

6. Prepare a decinormal solution of potassium sulphocyanate after the method outlined above (p. 178).

With the standard solutions of silver nitrate and sulphocyanate ascertain the concentration of a solution of ammonium chlorid by the method of residual titration. To 10 c.c. of the chlorid solution add 5 c.c. of the ammonium ferric sulphate indicator and 5 c.c. of dilute nitric acid. From a burette run in a few drops of decinormal potassium sulphocyanate, then, from another burette, enough decinormal silver nitrate to make the color of the liquid a pure white. If sufficient has been used, another addition of the sulphocyanate will give no red color. If it does, continue adding the silver solution until this condition is attained. The chlorid ion is then all precipitated as well as the whole of the sulphocyanate, and there is present an excess of silver nitrate. Now allow the sulphocyanate solution to flow in slowly from the burette with constant stirring until the red color, which disappears at first, is permanent. This indicates that both the chlorid and sulphocyanate ions are exactly precipitated. The difference between the volumes of silver nitrate and potassium sulphocyanate used gives the amount of decinormal silver solution which was required to precipitate the chlorid ion. From this the weight of the chlorin can be calculated.

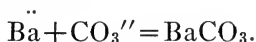
7. Determine the concentration of a calcium chlorid solution by making it alkaline with ammonium hydroxid, then adding ammonium carbonate solution as long as precipitation occurs and heating to boiling for a few minutes. Filter and wash with hot water until the wash-water is no longer alkaline. Then place the precipitate with the paper in a beaker with a small quantity of water. With methyl-orange as an indicator, titrate the liquid with normal hydrochloric acid until it changes to a permanent pink (acid) color. Calculate the percentage of the calcium salt in solution.

8. Mercuric chlorid when poured into a solution of potassium iodid forms a red precipitate (89). This dissolves, as it is stirred, as long as no more than one molecule of mercuric

chlorid is present for four of potassium iodid. When there is more than this the red precipitate is permanent. The mercuric solution must be poured into the iodid and not the opposite. By this means the metal or any mercury compound can be quantitatively determined provided it can be first converted into mercuric chlorid. A decinormal solution of potassium iodid, made by dissolving the weighed crystals in water, may be used as the standard and one-fourth the molecular weight of mercuric chlorid reckoned as present for each molecule of the iodid necessary to obtain the permanent precipitate.

9. Make a determination of the amount of ammonium nitrate in a solution of this salt which also contains ammonium sulphate, using the method given above (page 180) of converting the nitrate into a chlorid.

10. Neutral soluble salts of which the bases can be completely precipitated by sodium carbonate can also be estimated by the use of standard solution of the latter, the reaction being of the following type:



When the reaction of the liquid changes to alkaline it indicates that the cation has been precipitated. Salts of barium, strontium, and calcium can be quantitatively determined thus. To ensure the certainty that they are fully precipitated the liquid must be heated to boiling.

Find the concentration of a solution of barium nitrate, $\text{Ba}(\text{NO}_3)_2$, after the addition of a few drops of phenolphthalein solution, by titrating with normal sodium carbonate while the barium solution is at the boiling-point.

Questions for Further Study in Volumetric Analysis

What is the relation of the cubic centimeter to the gramme? Of the gramme to the liter? How many grammes in a liter

of water? Is this the same for all liquids? What is the best method of preparing standard solutions from very hygroscopic or efflorescent compounds? What are some of the most commonly used reagents of these classes? If a compound containing water of crystallization is to be weighed to make up such a solution how can it be determined whether the theoretical amount of water is present or not? In acidimetry which is determined, the cation or anion? Which in alkalimetry? What would be the best method for preparing a standard solution of ammonium hydroxid? Since both the standard sodium hydroxid and sodium carbonate have an alkaline reaction and will neutralize acids, why is it important to prevent the conversion of the former to the latter by carbon dioxide when it is to be used in a standard solution? Why cannot standard acids like hydrochloric, sulphuric, and nitric be prepared by accurately weighing the pure concentrated acid and diluting this with a known weight of water? Which ones of the common standard solutions are stable, and which must be standardized at each time of using? What is the nature of the blue compound formed by starch and iodine and what would be the effect of heating the liquid which contains it? Are standard solutions of reducing agents permanent or not? Why? Are those of oxidizing agents more or less permanent? Under what conditions are both best preserved? Why is ferrous ammonium sulphate selected for the standard solution of iron instead of crystallized ferrous sulphate? Given 10 grammes of dry, pure, sodium carbonate and the necessary measuring flasks, pipettes, etc., how can decinormal solutions of silver nitrate be prepared? of potassium permanganate? of sodium hydroxid? Starting in the same manner from 10 grammes of pure crystallized oxalic acid, how is it possible to prepare standard solutions of hydrochloric acid? of ferrous sulphate? of silver nitrate?

PART III

APPLIED ANALYSIS

CHAPTER I

THE SANITARY EXAMINATION OF WATER

ALL natural waters, whether known as well, spring, river, or cistern water, have been precipitated to the earth as rain and before they can be used have been brought into contact with so many soluble substances that they are never chemically pure. The purest form is rain water, but this contains in solution the gases of the atmosphere and often in addition small particles which floated in the air in the form of dust. If it has passed through or over the soil it contains more or less of the mineral, vegetable, or animal compounds with which it has been in contact. The dissolved gases are in general harmless and usually improve the taste of the water which without them is called flat or insipid. Of the other two classes of impurities—the mineral and organic—the mineral are much the less objectionable. Unless they are present in large quantities they produce little physiological effect. If the amount is sufficiently great to affect the system, the water is classed with the mineral waters which are so often used on account of their therapeutic value. Calcium and magnesium salts (principally the carbonate and sulphate) give to water the property commonly called “hardness,” that is, it does not dissolve soap, and consequently does not have the soft feeling that is characteristic of soapy water. It is also impossible to produce a permanent foam or lather with such hard water by shaking it with

soap solution unless a large amount of soap is added. Considerable quantities of mineral matters are objectionable where the water is to be used for making steam as it sometimes deposits as "boiler scale" and sometimes attacks the iron of the boiler. Compounds of lead, copper, or zinc should condemn a water, since they are poisonous, but they are rarely found in it. The chlorid ion is a valuable indication of the pollution of water. Sodium chlorid is found in soils where this has not occurred, but then, as a rule, only in very small quantities. The normal amount in any locality can be determined by testing the water from a number of sources in the region, and is practically a constant. As salt is always present abundantly in animal excreta and as it is soluble it will be taken up by any water that may come in contact with it.

Organic matter, vegetable or animal, in water may be considered dangerous, and when abundant should condemn the water for drinking. Unfortunately, the term organic matter does not mean one chemical compound, but rather a complex mixture of varying nature so that its identification is often a matter of some difficulty. This is especially true of the distinction between vegetable and animal substances, which are composed of the same elements and contain similar compounds. They, therefore, respond to the same test in many cases. They are, moreover, when contained in water, in a state of decomposition, becoming converted into other compounds. Thus the nitrogen, which is one of the characteristic elements of this mixed organic matter, appears after bacterial disintegration, first in ammonia, then in nitrites, and lastly in nitrates. Since none of the last three are found in common soil or air, except in traces, these may be assumed to indicate that the water contains, or has at some time contained, vegetable or animal matter.

Non-living organic matter in water may have deleterious effects upon the animal system from its own action or that of

its decomposition products, or it may serve as food for micro-organisms of which the pathogenic bacteria are the most important. These are thrown off in the excreta from many infectious diseases like typhoid and many can live a long time in water and communicate the disease by this means. Because of its frequent association with such organisms water which is contaminated with animal matter is regarded as more dangerous than that which contains a similar amount of vegetable products. Vegetable and animal substances remain if water is evaporated and when more highly heated they are discolored and blackened, often giving rise to offensive or characteristic odors. They are oxidized by potassium permanganate in the presence of sulphuric acid while they are in solution, the permanganate being at the same time decolorized. If the water has been proved free from nitrites or ferrous compounds, the action of which is the same, this may be considered a test for the presence of organic substances.

Qualitative Tests

Calcium and Magnesium

411. Make 50 c.c.¹ of water alkaline with ammonium hydroxid. If there is a precipitate of iron or aluminum hydroxid, remove it by filtration; otherwise to the liquid add ammonium chlorid and ammonium oxalate. A fine white precipitate of calcium oxalate forms slowly if but little calcium is present. If the precipitate is more than is obtained in the test for sulphates it indicates that a part of the calcium is probably in the form of a carbonate. Let it settle in a warm place, then decant or filter and test the filtrate for magnesium by the addition of sodium phosphate. A white crystalline precipitate of ammonium magnesium phosphate appears.

¹ The volumes of water directed to be used in tests may often be increased if the supply is large, thereby making the results more accurate. Except in quantitative tests they need not be accurately measured.

Iron

Examinations should be made for both the ferrous and the ferric forms.

412. To detect ferrous compounds add a few drops of a dilute solution of potassium ferricyanid and acidify with hydrochloric acid. A blue color is produced. The reagent does not react in this matter with the ferric ion. The ferric compounds may be shown to be present, after acidifying with hydrochloric acid, by the production of a red or pink color by the use of potassium sulphocyanate which remains colorless with the ferrous ion.

Poisonous Metals

413. Lead is the one which is most frequently suspected from its use in pipes, and occasionally it is desirable to test for copper or zinc. With any considerable quantity of the first two, hydrogen sulphid gives a brown or black color. It will usually be advisable before adding the sulphid to evaporate to about one-tenth of its bulk, as much as a liter of water after acidifying with hydrochloric acid, and the use of hydrogen sulphid gas is here preferable to its solution, to avoid dilution. If a black precipitate is obtained, it can be removed by filtration and identified by the method of Table IV. The zinc can be separated from the filtrate or, in absence of a precipitate with hydrogen sulphid, from the concentrated water by first making the liquid slightly alkaline with ammonium hydroxid, then passing in hydrogen sulphid and warming. It forms white, voluminous zinc sulphid which may be identified by its reactions.

Ammonia

414. Ammonia does not occur in natural waters in sufficient abundance to render possible its detection by its odor or by litmus paper. Very minute quantities, however, yield a

yellow to brown color with Nessler's reagent. If the amount is considerable there is a brown precipitate, but in ordinary waters the liquid remains clear. The result is somewhat complicated by the presence of calcium and magnesium compounds as they are in part precipitated at the same time. The difficulty can be completely overcome by distilling a part of the water from a retort and condensing the steam. The pure ammonia is found in the distillate.

In the detection of slight shades of color, or in estimating their intensity, the desired result can be best attained by using a test-tube placed above a piece of white paper and looking down into the tube.

Chlorin (the Chlorid Ion)

415. Acidify 30 c.c. of the water with nitric acid and add a few drops of a solution of silver nitrate. An opalescent or milky liquid is produced or, with large amounts of chlorin, a white precipitate of silver chlorid. This dissolves in ammonium hydroxid and is reprecipitated from this solution if it is acidified by nitric acid. Ordinarily there is too little chlorin to immediately give a curdy precipitate. If this is formed the amount is excessive.

Sulphates

416. Acidify 30 c.c. of water with hydrochloric acid and add barium chlorid. Fine white barium sulphate precipitates, settling slowly, and in very dilute solutions appearing only after standing some minutes. It is insoluble in acids.

Nitrous Acid or Nitrites

417. In the absence of ferric compounds the following may be used, but not if ferric salts are present. To 30 c.c. of water add two or three drops each of solutions of starch and potassium iodid, then acidify with about ten drops of

dilute sulphuric acid. Nitrous acid sets iodine free, which with the starch forms a blue color.

Ferric salts do not interfere with the next two tests.

418. Add to 30 c.c. of water, 1–2 c.c. of dilute sulphuric acid and 1 c.c. of a solution of meta-phenylen-diamin sulphate, which latter must be colorless. The appearance of a yellow to brown color indicates the presence of the nitrite ion.

419. Twenty c.c. of water with 2 c.c. of alpha-amido-naphthalene (naphthylamin) acetate and 2 c.c. of sulphanilic acid dissolved in acetic acid gives a pink or red color, varying with the amount of nitrites present. It should be allowed to stand five minutes to develop this fully.

The last two tests are much more sensitive than the first, so much so that extreme care must be used that neither they nor the vessels which contain the water are contaminated by nitrous acid from the atmosphere. The third test will detect one part of nitrous acid in one hundred million parts of water. On the other hand, if the starch test is distinct, in the absence of iron compounds, it is probable that a considerable amount of the nitrite ion is present.

Nitric Acids or Nitrates

If the nitrite ion has been found by the preceding tests it must be removed before examining for the nitrate ion as it will give most of the reactions for the latter. Evaporation of the water to dryness after the addition of a small pinch of ammonium chlorid decomposes the nitrites but not the nitrates.



The evaporation can be performed in a porcelain dish. To avoid the possibility of overheating at the last, when it has been reduced to a small volume it should be placed upon a beaker of boiling water and heated thus until it is dry. The residue can then be dissolved in pure water and the solutions

tested for nitrates. They will readily go into solution, although some of the other solids may remain.

420. To 30 c.c. of water add enough indigo solution to impart a pale blue color, acidify with sulphuric acid and heat to boiling. If nitrates are present the blue color is discharged or diminished.

421. In a porcelain dish containing 2-3 c.c. of water place a small crystal of brucin, then add an equal volume of concentrated sulphuric acid, stirring gently with a glass rod. A red color indicates nitric acid.

422. In the same manner as the last repeat the test using a small crystal of di-phenyl-amin instead of brucin. Nitric acid or its salts give a deep blue color. With one part in 100,000 it is seen immediately; when twice as dilute it may not appear for several minutes.

The test with indigo is not nearly so sensitive as the last two, but only responds when a considerable amount of nitrates are present. The concentrated sulphuric acid of the trade, even the so-called chemically pure, frequently contains nitric acid and should be proved to be pure previous to using in all the above tests. If not so, the nitric acid may be expelled by boiling for half an hour, until it remains colorless when tested with diphenyl-amin.

Hydrogen Sulphid

423. Acidify slightly 50 c.c. to 100 c.c. of water with sulphuric acid and boil for some time in a small flask in the neck of which is suspended a strip of white filter-paper previously moistened with a solution of lead acetate. A yellow or brown discoloration of the paper indicates hydrogen sulphid.

Organic Matter, Vegetable and Animal

Many animal and vegetable nitrogenous compounds are oxidized by potassium permanganate in alkaline solution with

a conversion of the nitrogen to ammonia. This, from its origin, is called albuminoid ammonia and in general indicates the amount of such nitrogenous compounds in the water.

Many of the organic compounds which are found in water are readily oxidized, even when dissolved, by such reagents as potassium permanganate. This loses its red color at the same time. A few inorganic substances have also the ability to decolorize permanganate, those which may be present in natural waters being sulphids, nitrites, and ferrous compounds. If these are absent or in very small amounts, water which decolorizes more than a few drops of a permanganate solution may be considered to contain some form of organic matter.

424. Acidify 50 c.c. to 100 c.c. of the water in a beaker or porcelain dish with 5-10 c.c. of dilute sulphuric acid, heat to boiling, and while hot drop in the permanganate solution until a permanent pink tint remains. Compare the result with that obtained in the same manner from a similar quantity of distilled water.

In addition to the decomposition products already discussed there are produced in water by bacterial processes small amounts of a number of compounds of which the most common are indol, phenol, and their derivatives. Griess has proposed a method of detecting these by the intensely yellow color which they yield with diazo compounds. They are very abundant in water which is polluted with decaying animal matter or animal excreta. They may, however, be formed by vegetable matter, their source being the protein compounds which are found in both, but less abundantly in the latter.

425. Make alkaline with sodium hydroxid 25 c.c. of water and add a few drops of a freshly prepared dilute solution of para-di-azo-benzene sulphonic acid. The liquid becomes yellow if the water contained decomposing animal matter or sometimes with large amounts of vegetable matter. The reagent cannot be preserved in solution, but must be dissolved

only when it is to be used. With the alkali and distilled water there should be thus produced no color, although this may occur if the sodium hydroxid is impure. A test should therefore first be made with distilled water to ascertain the purity of the reagents. This is Griess' test.

Quantitative Determinations

Total Solids

The amount of solid matter dissolved in a water is sometimes of importance. This can be ascertained by evaporating to dryness on a steam-bath a definite volume in a weighed dish and, after cooling, weighing the dish with the residue. With a sensitive balance 100 c.c. of water is enough in most cases, but if the balance will not weigh to a milligramme, more may be taken. A large amount of dissolved solids is indicative of contamination, although not conclusive. Mineral waters are, of course, an exception. The nature of the residue is indicated if it is more strongly heated after weighing. This is best done in a platinum dish, but may be accomplished in one of thin porcelain. Much organic matter will turn brown or black and may give a more or less characteristic odor. Mineral substances are not discolored, with the exception of iron compounds which may be brown. After the organic matter has burned off they can be dissolved in hydrochloric acid (except silica) and identified by their qualitative reactions.

Ammonia

The exact determination of ammonia is effected by distilling it from a large volume of water in a retort. The condensed steam contains the ammonia. By comparing the color produced in it by Nessler's reagent with that obtained by the same reagent in pure water to which has been added a known weight of ammonia, its amount can be estimated.

There are required a standard solution of ammonia and an alkaline permanganate solution. The standard ammonia solution is prepared by dissolving 3.82 grms. of pure ammonium chlorid in water and diluting to a liter. This contains a milligramme of ammonia (NH_3) in a cubic centimeter. For actual use it is better to dilute this 100 times. In the preparation of these solutions only ammonia-free water should be used—that is, water from which the ammonia has been removed by distillation or boiling.

[The alkaline permanganate solution is made by dissolving 8 grms. of potassium permanganate and 200 grams of potassium hydroxid in 1,200 to 1,500 c.c. of water and distilling until the remaining liquid is a liter and the distillate shows no test for ammonia.]

426. Connect with a condenser a 700–800 c.c. glass-stoppered retort which has the neck so bent that by inclining it upward drops spattered from the boiling liquid will run back into the retort and only the vapor will pass into the condenser. (The retort and condenser are connected as in Fig. 19.) Use 500 c.c. of water made alkaline by 3–4 c.c. of sodium carbonate solution freed from ammonia by previous boiling. A few pieces of pumice stone ignited and dropped while hot into the retort makes the distillation proceed more quietly.

Collect the distillate in large test-tubes or flat-bottomed Nessler tubes in portions of 50 c.c. each, adding to each 2 c.c. of Nessler's reagent. Drop from a burette into ammonia-free water enough of the standard ammonia solution to give the same shade with Nessler's reagent when, after standing five minutes, it has been diluted to 50 c.c. In this manner the amount of ammonia in each portion is learned. The *free* ammonia should be all expelled with the first 200 c.c. Then discontinue the heating and pour in 50 c.c. of the alkaline permanganate solution; continue the distillation and Nesslerizing as before as long as ammonia is driven off. This

portion is the *albuminoid* ammonia and represents the undecomposed nitrogenous organic matter.

Chlorin (the Chlorid Ion)

427. To determine the quantity of chlorin use a standard solution of silver nitrate with normal potassium chromate for the indicator, as described on page 180. For convenience in calculating results instead of the usual concentration the silver solution may be made to contain 4.79 grammes of silver nitrate per liter. One cubic centimeter of this will precipitate one milligramme of chlorin. Of ordinary well-water 100 c.c. may be used. In this case each cubic centimeter of the silver solution necessary indicates one part of chlorin in 100,000 of water. With water of great purity it may be necessary to concentrate a larger volume, such as a liter, before titrating.

Nitrites (the Nitrite Ion)

When solutions of nitrites are treated with sulphanilic acid and naphthylamin an intense rose-red color appears varying with the amount of the nitrite ion present. By comparing it with a solution of nitrite of known strength it is not difficult to judge the amount of the latter.

The reagents used are:

Sulphanilic acid, 0.5 gram. dissolved in 150 c.c. of 3 per cent. acetic acid, and

Alpha-naphthylamin, 0.1 gram. of the solid boiled with 20 c.c. of water and filtered hot through a small filter, previously well washed to remove nitrites, then the filtrate diluted with 180 c.c. of 3 per cent. acetic acid.

Standard sodium nitrite, 0.049 gram. of pure sodium nitrite dissolved in one liter of water.¹ One cubic centimeter of this contains 0.01 milligramme of nitrogen. If it cannot be ob-

¹ Since this would be difficult to weigh accurately it is better to dissolve 0.49 gram. in 100 c.c. and dilute 10 c.c. of this to 1000 c.c. before using.

tained pure in the dry state it can be made by dissolving the corresponding weight (0.113 gm.) of silver nitrite in a small volume of water and adding a solution of pure sodium chlorid as long as a precipitate forms, then diluting to the desired amount. It must be kept in the dark. The reagent bottles and all vessels used in the test must be rinsed with nitrite-free water.

428. To exactly 10 c.c. of the water in a test-tube add 1 c.c. each of the solutions of sulphanilic acid and naphthylamin and allow to stand five minutes. If it is pink, in another test-tube dilute 1 c.c. of the standard nitrite solution to 10 c.c. and test in the same manner. Dilute the darker of the two until equal volumes are the same shade and from the amount of dilution calculate the amount of nitrite in the water as compared with that of the standard, and from this, the absolute weight of N in nitrites in 10 c.c. and in a liter. Reduce this to parts per million remembering that one milligramme per liter equals one part per million.

Nitrates (the Nitrate Ion)

The nitrate ion can be quantitatively determined by its action upon phenolsulphonic acid, which is changed into picric acid, the ammonium salt of which has an intensely yellow color. Besides a standard solution of a nitrate for comparison but one other is needed.

Phenolsulphonic acid is prepared by heating for an hour or two on the water-bath 25 grams of phenol (carbolic acid) with a mixture of 150 c.c. of concentrated sulphuric acid and 75 c.c. of fuming sulphuric acid, stirring occasionally. The solution keeps well. If it in time crystallizes it can be redissolved by warming gently.

Standard potassium nitrate can be made by dissolving of this salt 0.722 gm. in a liter of water. One c.c. of this contains 0.0001 gm. of nitrogen.

429. Evaporate to dryness on a steam-bath a definite vol-

ume of the water—25 to 100 c.c. according to whether the qualitative test showed much or little nitrate present. If much chlorin has been found it is best to remove it by precipitation with nitrate-free silver sulphate and filtration. To the residue add 1 c.c. of phenolsulphonic acid and, after thoroughly mixing, let it stand two or three minutes, then add 20 c.c. of water and make alkaline with ammonia. Treat 1 c.c. of the standard solution in the same manner and compare the colors in large test-tubes, diluting until they are the same and computing the amount of nitrogen in the nitrates in parts per million as with nitrites above. In the whole process the distilled water and sulphuric acid used must be known to be free from nitric acid and its salts, as discussed under the qualitative tests.

Organic Matter

The amount of this can be only indirectly determined because of the variable nature of that which may be present. The degree of discoloration or charring, also the odor, of the heated residue after evaporation may give some indication of it. Other methods are to determine the exact quantity of organic carbon or nitrogen (as in 426) in the water and to use them as measures of the vegetable and animal matter. Instead of these it is more convenient to find the amount of oxidizable matter and, deducting the nitrites and ferrous compounds, also the sulphids, if they are present, to regard the remainder as organic. A suitable oxidizing agent for this purpose is a solution of potassium permanganate which readily gives up its oxygen in an acid liquid, becoming at the same time colorless.

430. A rough estimate can be made of the amount of oxidizable matter by acidifying 50 or 100 c.c. of the water with 10 c.c. of dilute sulphuric acid, heating to boiling, then counting the number of drops of centinormal potassium permanganate necessary to color the boiling liquid permanently pink. The reagent can be dropped slowly if the stopper is held loosely

without removing it from the bottle. For comparison the same test may be tried on an equal volume of distilled or other pure water.

431. For more accurate results a centinormal solution (0.316 gm. per liter) of potassium permanganate may be used with a corresponding one of oxalic acid, so that one cubic centimeter of the latter shall decolorize exactly one of the former. To 100 c.c. of the water in a 250 c.c. flask add 20 c.c. of dilute sulphuric acid, then from a burette, 10 c.c. of the permanganate or enough to give permanent red color to the water after it has been boiled 10 minutes. This should be accurately measured. When it has been boiled 10 minutes add from another burette a volume of centinormal oxalic acid equal to that of the permanganate used, when the red will disappear. Now drop in more permanganate from the first burette, while stirring, until a permanent pink color is produced. The volume of permanganate last added corresponds to that destroyed by the oxidizable substance in the water. Ten cubic centimeters contain 0.08 milligramme of available oxygen, and the final results should be expressed in terms of this.

Owing to the fact that there is a great variation in the ease of oxidation of different kinds of organic matter as well as in their content of carbon and nitrogen, the results obtained should be regarded as only approximate although they are often of great value in arriving at a conclusion as to the purity of the water. For the properties of the standard solutions of permanganate and oxalic acid reference should be made to their description under Oxidimetry.

Interpretation of Results

Calcium, magnesium and iron are comparatively unimportant in water from the sanitary standpoint, although when excessive they greatly lessen its value for domestic purposes,

the first two because they render it hard, and the last because it deposits as a brown ferric hydroxid. They all more or less modify the taste. The sulphate ion, as found in sulphates, if united with the calcium makes the water permanently "hard," that is, this compound is not precipitated by boiling, as is the carbonate. Small amounts of sulphates are otherwise not of much consequence, although considerable quantities of sulphates cause the water to act as a laxative.

It is only exceptionally that ammonia is absent from natural waters. It signifies that, probably by bacterial action nitrogenous organic compounds, vegetable or animal, have been decomposed, the latter yielding more than the former. When nitrites are found, bacterial action upon these compounds is in progress, although the bacteria are not necessarily of the pathogenic varieties. Nitrates are the final products of such action, unless they are again reduced to nitrites. When found alone they indicate some past pollution by nitrogenous substance—animal or vegetable. Chlorin occurs rather abundantly in the soil near the sea and in parts of the country where there are salt deposits or brines. If then loses much of its value as an indication of contamination. Since, however, water drawn from the same stratum in the same section has practically the same composition unless it is contaminated, a comparison of the amount of chlorin in the water of one well with that of surrounding ones will often show whether it is excessive or not. Neglecting that of the soil, it is an evidence that pollution has occurred from animal matter, probably sewage. This is of course pollution of the most dangerous kind; still if chlorin alone is found it may be that the accompanying organic matter and bacteria have been filtered out by the soil, or oxidized by the air, and that the water will not communicate disease; in other words it is an evidence of past contamination. The chlorid ion in itself has no poisonous action, but its presence is suspicious. Hydrogen sulphid can be pro-

duced by the breaking down of organic sulphur compounds like the proteins, or by the action of decomposing organic matter on the sulphates, whereby the latter are reduced. Hence it usually shows that considerable organic matter is, or has been, contained in the water.

Decolorization of the potassium permanganate solution, in the absence of reducing agents like nitrites, sulphids, or ferrous compounds, indicates organic matter, either animal or vegetable. Para-diazo-benzene-sulphonic acid in alkaline solution (Griess' test) shows the presence of compounds such as result from the putrefaction of albuminous matters. These are abundant in the excreta and decaying animal tissues, but may be produced also from similar changes in the vegetable albuminous substances. In the last case they are only found in comparatively small amounts.

We might then expect to find in water containing fresh vegetable matter a little ammonia and some reduction of the permanganate solution, but no reaction to Griess' test and an absence of more than traces of chlorin, nitrites, and nitrates. As the organic matter decays the ammonia increases and the reduction of the permanganate diminishes until there may be none. There will finally be a conversion of most of the nitrogen into nitrates with possibly a slight amount of nitrites. It is seldom that all the ammonia disappears.

Animal matter (excreta or tissues), while decomposition is in progress, reduces the permanganate solution and gives Griess' reaction if in sufficient quantity. Chlorin and ammonia are then abundant, nitrites are often present and sometimes nitrates. As the decomposition progresses the permanganate and Griess' test give less marked results and the nitrates increase. The quantity of chlorin is not affected.

The source of the water will also somewhat modify the conclusions to be drawn from the analysis. Thus deep well water often contains much chlorin from the rock formations with

which it comes into contact. More ammonia may be allowable here than in surface or shallow well waters since it has no means of escape and the conditions are unfavorable for bacterial life. It is produced here by the reduction of nitrates through the action of organic matter. Nitrates are occasionally found plentifully in deep waters, being derived from the remains of fossil organisms. This is especially seen in cretaceous rocks. On the other hand, organic matter is usually absent or in traces. Rain water absorbs much ammonia and sometimes nitrites from the air and these then lose their customary significance, being no longer indicative of organic decomposition. In the water from deep wells (artesian) also nitrites may be formed through the reduction of nitrates by organic matter without the aid of bacteria and then are unimportant.

Standards of Comparison

From what has been said regarding the modifications which surrounding conditions produce in the composition of water it is obvious that we cannot establish any absolute standards which shall apply to that from all sources. Nevertheless, it is a matter of great convenience to be able to compare the composition of one under observation with that of others, the nature of which has been determined. Such figures must be used carefully with a full understanding of the influences that may change them. Knowing, then, that the standards represent only the amounts of impurities which have been found to be present in other cases, we can employ them as aids to the formation of an opinion as to the significance of our analyses.

The following may represent the composition of some varieties of drinking-water in which the figures represent parts per million.

	Good, less than	Suspi- cious.	Bad, over	Milligrams per Liter.	= Parts per Million.
Total solids,	500	500-700	800		
Chlorin,	5	10-15	25	NaCl, 2.3	Chlorin, 15.
Nitrogen in nitrites,	0	0.02	0.04	NaNO ₂ , 0.1	Nitrogen in nitrites, 0.02.
Nitrogen in nitrates,	0.5	1.0-2.0	5	KNO ₃ , 14.0	Nitrogen in nitrates, 2.0.
Free ammonia,	0.03	0.05-0.1	0.15	NH ₄ Cl, 0.3	Ammonia, 0.1.
Albuminoid ammo- nia,	0.1	0.1-0.15	0.2		
Cubic centimeters of N 100 KMnO ₄ reduc'd by 100 c.c. of water,	1.5	3-4	8		

Solutions made up of the above concentrations by the aid of the last two columns, may serve for comparison so that the more accurate quantitative methods of determination can at times, be dispensed with.

Practical Exercises in Water Analysis

Make chemical examinations of samples of water furnished by the instructors. Hand in written reports giving the presence or absence, also comparative amounts (small, moderate, or large) of the following:

1. Calcium.
2. Magnesium.
3. Iron, ferrous and ferric.
4. Lead, copper or zinc.
5. Ammonia.
6. Chlorin.
7. Sulphates.
8. Nitrites.
9. Nitrates.
10. Organic matter by general tests.

Give an opinion as to the past history of the water. If it contains organic matter, is this vegetable, decaying animal or sewage? Is the water suitable for drinking, to be condemned, or merely suspicious? Is it suitable for other purposes than for drinking? Give reasons for your conclusions.

CHAPTER II

THE DETECTION OF POISONS

THE testing of substances for the detection and identification of poisons, although it may be properly considered in a separate chapter from general analytical chemistry, is not a different branch of chemistry, but makes use of many of the principles and operations already considered.

Its importance lies in the value of the evidence of the chemist as a proof of attempted or accomplished poisoning, and in the fact that this is often the strongest, and sometimes the only, evidence obtainable. It differs from the more common methods of analysis in the nature of the materials which are investigated, these being often complex mixtures of organic and inorganic compounds, such as medicines, foods, vomited matter, saliva, urine, blood, or animal tissues. In these the poison sought is ordinarily comparatively very small in amount. Not only must the presence of a poisonous element be shown, but that it is in a combination dangerous to the animal body. For example, most sulphates are harmless, whereas the acid from which they are derived is a violent poison. It is, moreover, frequently desirable to determine not only the kind but the amount of such compounds in the substance analyzed.

Some of the difficulties encountered in testing for poisons are that their minute amount renders many of the common reagents ineffective, that the presence of other compounds, especially organic matter, interferes with their giving the expected reaction, that their separation from such compounds and purification requires much time and care, that during the necessary operations they may volatilize, as does prussic

acid, or undergo decomposition, like the alkaloids, or become converted into a harmless form as may be phosphorus. Still, for many of them, the means of identification, if properly carried out, are as effective as any analytical processes.

Since but a limited quantity of the substance is at the disposal of the analyst the tests should be applied at first to only a portion in order to have a reserve in case of accidents, or for further investigation, and it is better to note the weight of the whole and of the part used in order to be able to calculate the total amount present from the fraction that may be found in that part. To avoid a waste of material the most characteristic and reliable tests should be tried first. If possible the isolated poison or compounds of it should be preserved in such a way as to be submitted in a possible future trial.

The question of the purity of the reagents is of the greatest importance. The different grades of "purified," "pure," "chemically pure," and "absolutely chemically pure" do not necessarily guarantee the same quality when they are made by different manufacturers. It will be necessary to prove their purity or to make with them a blank test—that is to go through the operation with the chemicals alone without the addition of the suspected substance, when, if they are of satisfactory quality, the result should be a negative one. The reagents in common use may suffice for the usual methods of testing and fail to give satisfaction when a hundred or a thousand times the ordinary quantity of them must be employed. All other materials, such as filter-paper, rubber tubing, or apparatus, must also be known to be free from objectionable substances.

There follows a list of the reagents of most frequent use in toxicological investigations, with a discussion of their impurities.

Water

This should of course be distilled, but as occasionally such water contains traces of the heavy metals it should be

tested by evaporating a liter to dryness. There must be left only a minute residue and this, after dissolving in 5-10 c.c. of water must give no precipitate with hydrogen sulphid or ammonium sulphid. Distillation is best conducted in a tin-lined vessel and the steam condensed in a tin pipe.

Hydrochloric Acid

This should, after dilution give no precipitate upon saturation with hydrogen sulphid or, after neutralization, with ammonium sulphid. Its most dangerous contamination is arsenic which is not infrequent. Very large amounts of the acid are used in the destruction of organic matter and hence a comparatively large quantity of arsenic may be introduced even if but a small fraction of a per cent. is contained in the acid. It cannot be regarded as of satisfactory purity unless after about a liter is concentrated to a small volume (10 to 20 c.c.) by evaporation in a well-ventilated hood and 5 c.c. of the remaining liquid is tested with Gutzeit's test (109) no yellow color with brownish-black margin appears on the paper within half an hour. It may be further tested by Bettendorf's (111), Reinsch's (108), or Marsh's (112) tests.

Sulphuric Acid

This is not used in such large amounts as the hydrochloric, and there is consequently less danger of introducing impurities with it. Its principal use is in Marsh's test for arsenic. It occasionally contains lead as well as arsenic. The lead will be shown by the yellow or brown color produced by saturating the dilute solution with hydrogen sulphid gas. For arsenic it can be tested, after diluting with four times its volume of water, by Gutzeit's (109), Reinsch's (108), or Marsh's (112) tests. With the latter 200 c.c. of the acid, generating about a liter of hydrogen in fifteen minutes should show no mirror in the tube after half an hour's heating.

When used in the alkaloidal tests it must be absolutely free from nitric or nitrous acid. Hence it should give no color with brucin (421) or di-phenyl-amin (422). These compounds if present may be removed by boiling as in 422.

Hydrogen Sulphid

The materials commonly used in the preparation of hydrogen sulphid frequently contain arsenic. Either those which are free from arsenic should be employed or the gas must be purified. Passing it through a long tube over crystals of iodine forms arsenic iodide which remains in the tube.

Ammonium Sulphid

This must be prepared from arsenic-free hydrogen sulphid, made in the above manner.

Ammonium Hydroxid and Sodium Hydroxid

Arsenic and the heavy metals should be absent. When acidified with pure sulphuric acid no results should be obtained from Marsh's test, from the addition of hydrogen sulphid, nor after making alkaline by ammonium sulphid.

Potassium Chlorate

This should be free from arsenic and the heavy metals. Dissolve 50 grammes in water and add pure hydrochloric acid as long as chlorine is evolved. Test half the solution by Marsh's test (112) and the rest by hydrogen sulphid (Table IV) and ammonium sulphid (Table II).

Ethyl Alcohol

Metals and other basic substances must be absent. By distilling over tartaric acid they can be separated if small amounts are present.

Amyl Alcohol

It should leave no residue when evaporated, should boil at 131° – 132° ; and when shaken with dilute sulphuric acid should give to the latter nothing which gives the general alkaloidal reactions (page 139).

Benzene

This should have the boiling-point of 79° and otherwise answer the requirements of amyl alcohol.

Chloroform

Can be tested as the last. It should boil at 61° .

Petroleum Ether

The boiling-point should not be above 60° . No residue should remain when it is allowed to evaporate on a watch glass.

The filter-paper employed should be white and the ash remaining after it is burned should be little and free from barium and the heavy metals. When the solutions must come in contact with the rubber tubing this should contain none of the poisonous metals. In the white tubing lead and zinc are often found, and in the red, antimony. Black rubber is the preferable kind. Porcelain vessels are less liable to break than glass ones, also to attack by reagents, but they should not be used after the enamel is in any degree injured, and the enamel must contain no lead.

Outline of the Plan of Analysis for Poisons

I. Preliminary examination.

II. Distil in the presence of an acid with the aid of steam the volatile poisons, hydrocyanic acid, phenol (carbolic acid), phosphorus, chloroform, chloral hydrate.

III. Extract the residue with alcohol.

1. The alkaloids.
2. Oxalic and meconic acids and some mercury salts.

IV. Destroy the organic matter and test the solution for metals of which the compounds are poisonous.

I. Preliminary Examination

Before proceeding to the systematic analysis a preliminary examination will be advantageous. This may be both physical and chemical. In the former, if the material is a complex mixture, like the contents of a stomach or vomited matter, its appearance should be noted, as to whether there is evidence of the presence of unusual substances. Sometimes the unaltered poison (vegetable or animal) may be thus detected. A low-power magnifying glass is of service. Phosphorus will be visible if the room is darkened, especially after the substance is dried and stirred in the air. Any odors should be noticed, as they may be characteristic of some compound sought. Not more than one-tenth of the available material should be destroyed in preliminary tests.

Reaction.—A strong acid or alkaline reaction to litmus paper may be due to mineral or oxalic acids or to a caustic alkali.

The above acids will be found in the aqueous extract and change a Congo-red solution to a deep blue. Oxalic acid changes the color of a methyl-violet solution to a blue. Hydrochloric acid of the concentration found in normal gastric juice will do the same, also very dilute solutions of nitric or sulphuric acids. In any considerable amount the last three give with methyl-violet a green to yellow color. If a few cubic centimeters of the solution be slowly evaporated from a small test-tube with a few crystals of cane-sugar there will be with sulphuric acid a blackening or charring as the water is driven off; with nitric, an evolution of yellowish-brown oxids

of nitrogen; with hydrochloric, a yellow, then brown color in the liquid, with the odor of the acid gas; with oxalic acid, no odor or colored gas, nor discoloration until the water has been expelled, when the sugar will be converted to caramel if the heating is continued.

Of the caustic alkalies ammonium hydroxid will have already been recognized by its odor although it must be remembered that ammonia may be formed by the bacterial decomposition of nitrogenous matter. The sodium hydroxid and potassium hydroxid can be dissolved from dried residues by hot alcohol. They remain after this has been distilled. Solutions of these turn litmus-paper blue and give a red color to a phenolphthalein solution. The alkaline carbonates do the same, but not after an excess of barium chlorid has been added to the solution. The alkaline hydroxids will act upon litmus and phenolphthalein after the addition of barium chlorid as well as before.

Test for phosphorus and hydrocyanic acid in a partly filled flask with lead acetate paper (437) and silver nitrate paper (437), also guaiacum paper (432) and watch-glass tests (433 and 436).

Dialysis of a portion of the mass may render possible the classification of the poison. Place the substance in a dialyzer,¹ after thinning with water and slightly acidifying with nitric acid, and let this stand 24 hours in four or five times its volume of water. The liquid outside is then concentrated, if desirable, and examined for some of the groups of poisons, one portion being tested by hydrogen sulphid for the heavy metals, another for the alkaloids, by means of the general reagents (page 139), another for the acids of alkalies, etc.

¹ The dialyzer may consist of a wide glass tube which has one end closed with a membrane of animal or vegetable parchment. The substance to be dialyzed is placed in this and the whole is suspended in a vessel of water so that the level inside and out is the same. Or, instead of this, a parchment tube containing the substance may be suspended from the ends in the water.

If in the preliminary tests some indication has been obtained of the class of compounds the search should be made first for these. If no indication had been obtained of the class to which the poison may belong a systematic examination must be undertaken for all that can be present. For this the remaining material may be divided into four parts and one

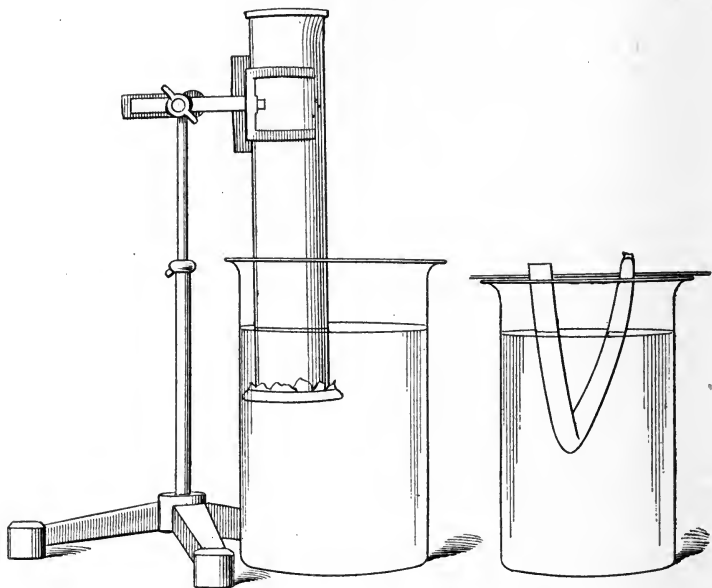


FIG. 18.—Two forms of dialyzers; the first an open glass tube with parchment end, the second a tube of parchment paper.

examined for each class of compounds unless the poison is found sooner, one being reserved for emergencies or confirmatory tests. The plan of analysis given will serve as a general guide for work, although the chemist will often modify it in accordance with his observations during the progress of the analysis. It is far from including all poisons, but it may be used in the search for the more common. For a complete

course of analysis reference should be made to some larger work, such as that of Haines and Petersen or Dragendorff.

II. Poisons Distilled from an Acid Liquid

Dilute the finely divided mixture into a thin fluid with water, then add enough dilute sulphuric acid to merely give an acid reaction. Distil from a retort on a water-bath, toward the last of the operation passing in steam from a flask through a tube which extends nearly to the bottom of the liquid. The distillate must be well cooled by a long Liebig's condenser.

Hydrocyanic Acid

(Ferrocyanids and ferricyanids must be absent, or the tests are not conclusive).

The volatile acid has the characteristic odor of bitter almonds, and appears in the first stages of the distillation.

432. The gas or a drop of the distillate turns blue a white paper previously moistened with very dilute copper sulphate solution and an alcoholic solution of guaiacum resin. There are a few other substances which give a similar result, but they are not commonly present.

433. With silver nitrate a white precipitate is produced, which dissolves in ammonium hydroxid or sodium hydroxid and is reprecipitated therefrom by nitric acid in which it is insoluble. It is not discolored by light like silver chlorid (225). To remove any hydrochloric acid which may have been distilled over from the retort, before testing with the silver nitrate, the distillate can be shaken with a little powdered borax and redistilled. For very minute quantities spread a drop of the silver nitrate solution over the convex surface of a watch-glass, letting this stand over a similar glass containing the hydrocyanic acid.

434. The distillate forms Prussian blue with iron salts when treated according to 233.

435. To a few drops of the distillate add 2 or 3 drops of a solution of potassium nitrite and as much ferric chlorid. Drop in dilute sulphuric acid until the brown color becomes

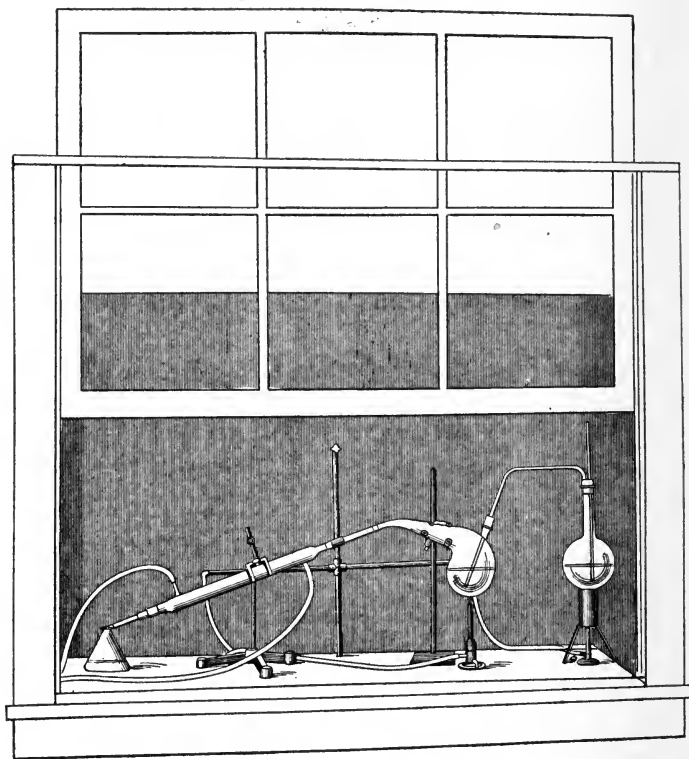


FIG. 19.—*Apparatus for distillation with the aid of steam.* This is passed into the liquid in the retort by a tube which enters through the tubulure. The flask at the right in which the steam is generated is provided with a straight safety-tube, open at both ends. This allows air to enter if the heating is interrupted and thus prevents the liquid in the retort from being drawn back. The neck of the retort is connected with a Liebig's condenser and the whole apparatus stands in a hood which is provided with a flue and a sliding door so that obnoxious gases are removed from the room.

a yellow and warm gently. Cool, precipitate the iron with a few drops of ammonium hydroxid, filter, and to the filtrate

add one drop of very dilute ammonium sulphid. A violet color appears, changing to blue, green, and yellow. The hydrocyanic acid has been converted into a nitroprussid which gives the above results with sulphids. Less than one part in a million can be thus detected.

436. Place between two watch-glasses as in 433 adding H_2SO_4 for a cyanid. Moisten the under surface of the upper glass with yellow ammonium sulphid solution and allow to stand 10 minutes. Ammonium sulphocyanate is formed on the upper glass. Remove this and dry on a water-bath. Very dilute ferric chlorid gives a red color with the residue after acidifying with HCl (57).

Phenol (Carbolic Acid)

As this is less volatile than the hydrocyanic acid, the latter portion of the distillate can be used for testing. With this try the phenol reactions (page 127).

Chloroform

If much is present it will appear as colorless drops with the characteristic odor, unless the latter is hidden by other compounds. Try the test with anilin and potassium hydroxid (259) and, if necessary, confirm by 260.

Chloral Hydrate

The distillate gives no odor of chloroform until it has been warmed with an alkali. Test with resorcin (301), ammonium sulphid (302), or with sodium hydroxid (298).

Phosphorus

Carry on the distillation in a perfectly dark room. Notice the luminous ring in the condenser (438). For a confirmatory test use the color of the flame with hydrogen generator (439), also effect on silver nitrate paper (437) as directed below.

The yellow variety of phosphorus is the one which acts poisonously. Its odor and luminous appearance in the dark are characteristic.

437. When an acidified liquid or mass containing phosphorus is placed in a flask of such a size that it shall be at least three-fourths filled with air and from the loosely inserted stopper strips of filter-paper are hung which have been moistened, one with a solution of lead acetate made alkaline with sodium hydroxid, and the other with silver nitrate, the latter is darkened slowly by the reduction of the silver salt by the vapors of phosphorus. The former is unaffected. Hydrogen sulphid blackens both papers and its presence destroys the value of the test unless it is held in the solution by the use of sodium hydroxid. Failure of the paper to darken indicates the absence of phosphorus. The flask should be allowed to stand a considerable time in a dark place before the conclusion of the test.

438. If a mixture containing phosphorus is diluted with water then, after acidifying, is placed in a retort and distilled in a dark room by passing steam through it, the vapors being cooled by a Liebig's condenser, at the point where the steam is condensed there appears a phosphorescent ring. This moves back and forth in the condenser and may be visible a long time. Very minute amounts of phosphorus may be thus detected, but the phosphorescence is prevented by mercuric chlorid, alcohol, and some other volatile substances. It appears, however, when these latter have been removed.

439. When treated in a Marsh's apparatus, as described in the test for arsenic (112), phosphorus forms hydrogen phosphid, PH_3 , which, when passed into silver nitrate solution, forms dark, insoluble silver phosphid mixed with metallic silver. This compound can be filtered out and tested, after acidifying, by distillation as above. If the gas is passed through a tube filled with pieces of pumice saturated with

sodium hydroxid for the purpose of absorbing the hydrogen sulphid which may be present, the flame of the ignited gas is greenish. It should not be lighted until the air has been completely expelled and should be burned from a small metal tube, for instance, a mouth blowpipe, to avoid the color which the sodium of the glass would impart. The color can be made more perceptible by holding a cold porcelain dish in the flame.

III, 1. Examination for Alkaloids

To another portion of the finely divided mass add so much dilute sulphuric acid that the reaction is faintly acid (but not more than 5 c.c. of 20 per cent. acid for each 100 c.c. of the liquid). Mix thoroughly and let it stand several hours at 40° to 50°, then filter through a cloth. Repeat the extraction, uniting the filtrates. Evaporate on a steam-bath to a thin syrup, but no farther; dilute with 3-4 times its volume of 90-95 per cent. alcohol, which dissolves the alkaloidal sulphates, and filter after it has stood 24 hours. Pour the filtrate into a flask and distil off the alcohol on a steam-bath. The sulphates of the alkaloids remain. Test a portion for these, reserving some for III, 2; III, 3; and III, 4.

The alkaloids and some other organic poisons can be, to some extent, classified and separated by the differences in solubility of their salts and the free substance in certain organic solvents. When the aqueous liquid is mixed, without too violent shaking, with the solvent and the mixture is allowed to stand, the solvent, which is selected so as to be lighter or heavier than the original fluid, removes from this liquid the alkaloid. By performing this operation in a separatory funnel or a burette with a glass stop-cock one liquid can be separated from the other. To ascertain if anything has dissolved, or to test it, a drop of the solvent after separation can be

allowed to evaporate on a watch crystal. The steps in this separation are:

(a) If necessary add water until the acidified solution is not syrupy, then shake in a separatory funnel with petroleum ether, repeating until the soluble matter has been dissolved.

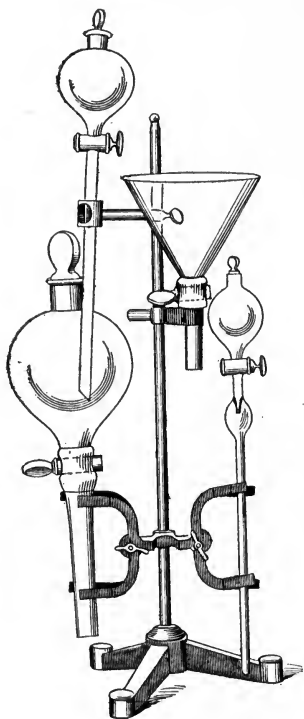


FIG. 20.—Different forms of separatory funnels used for separating a liquid from another in which it is insoluble.

The petroleum ether contains some of the coloring matters, also the fats, and the phenol which was not removed by distillation.

(b) To the solution from which the petroleum ether has been separated add sufficient ammonium hydroxid to make it strongly alkaline. The alkaloids are set free and, if in large amounts, may appear as a precipitate. Whether this is so or not, shake the liquid with more petroleum ether, separating as before, after standing long enough for the petroleum ether to have completely risen to the top of the aqueous solution. If a residue remains when the petroleum ether has spontaneously evaporated in a watch-glass, it may be cocaine which is in white crystals. If such a residue remains treat the liquid with the petroleum ether as long as a drop leaves any solid

when evaporated. Test the residues by the cocain reactions (page 144).

(c) In the same manner shake the remaining solution from the petroleum ether extraction with benzene (benzol, C_6H_6)

letting the benzene evaporate on a number of watch-glasses without heating. To learn if an alkaloid is present dissolve in water with a drop of acid and apply the general alkaloidal reagents (page 139).

There may be contained in the residues from the benzene atropin, brucin, narcotin, strychnin, and veratrin. Observe the appearance and, if the general alkaloidal reagents (page 139) show the presence of alkaloids, test the separate portions with a drop of concentrated sulphuric acid and another of concentrated nitric acid.

	Usual Form.	H ₂ SO ₄ , Concentrated.	HNO ₃ , Concentrated.	Tests on Page.
Atropin,	crystalline,	colorless,	colorless,	143
Brucin,	amorphous,	colorless,	deep red,	142
Narcotin,	crystalline,	colorless,	yellow,	141
Strychnin,	crystalline,	colorless,	yellow,	141
Veratrin,	amorphous,	yellow, orange, then red (396)	yellow to colorless.	144

Confirm the indicated alkaloids by the individual reactions.

(d) The solution which has been treated with benzene is to be shaken with amyl alcohol and, after separating, the latter is to be evaporated on the steam-bath.

Morphin remains as a crystalline residue. Confirm it by its characteristic reactions (page 140).

III, 2. Examination for Oxalic Acid

A part of the alcohol solution from the dried substance is filtered and evaporated to dryness on the steam-bath and the residue dissolved in water. This solution, if oxalic acid is present, gives calcium oxalate with calcium chlorid (176); it decolorizes potassium permanganate (177); oxalic acid precipitates from a solution of gold chlorid metallic gold in scales (133). Other tests have been referred to in the preliminary examination.

III, 3. Examination for Meconic Acid

Test with silver nitrate (315) and ferric chlorid (314). The latter is the more characteristic.

III, 4. Examination for Metallic Compounds Soluble in Alcohol, Especially those of Mercury

Although the general tests for the metallic compounds are made with another portion of the substance, this solution may be tested with hydrogen sulphid and the test completed in the usual manner (Table III). Since only substances soluble in alcohol can be present here the discovery of a metal affords some indication of the original compound.

IV. Metallic Poisons

They may include compounds of arsenic, antimony, lead, copper, mercury, silver, zinc, and barium.

These may be sought in the residue from the alcoholic extraction of III (except lead and barium) or another portion of the mass under investigation. In order to obtain them in a sufficiently pure state to identify them any organic matter present should be first destroyed. This is accomplished through oxidation by means of chlorin. The finely divided mass is diluted to a thin mixture with pure, concentrated hydrochloric acid, and a little water. Place it in a flask which it must no more than half fill, and drop in from time to time a little powdered potassium chlorate as long as the fluid has a dark color, assisting the oxidation toward the last by warming on the steam-bath. Avoid the use of unnecessary amounts of either acid or chlorate. Cellulose or masses of fat, which are difficult to decompose, may be filtered out and the filtrate employed for the examination.

The clear liquid is freed from chlorin by passing carbon

dioxid through it and afterward saturated with hydrogen sulphid. This may be done in a flask fitted with a two-holed rubber stopper and two tubes. The entrance tube is connected with the generator and extends to the bottom of the solution. Gas is passed in for 24 hours (102), the liquid being warmed and shaken occasionally. The zinc and barium alone remain unprecipitated. Filter and wash.

Compare the color of the precipitate with that of the sulphids of metals possibly present. Separate or test it by the methods given in Table IV, confirming by the reaction of the individual metals, using for the latter purpose a fresh portion of the solution if desirable.

Test the filtrate for zinc after the method of Table II and the zinc reactions (page 39). If this is not present or has been removed, test for barium according to Table I and the barium reactions (page 30).

Special Problems in Toxicology

Detection of Arsenic in Milk or Liquid Foods.—Use Reinsch's test (108).

Detection of Arsenic or Lead in Urine.—Acidify about a liter with hydrochloric acid, saturate with hydrogen sulphid gas and let it stand in a corked flask for 24 hours. If there is a precipitate, filter and wash it. If it is yellowish, test for arsenic by Gutzeit's test (109). If black dissolve in a few drops of nitric acid and test for lead (147, etc.).

Detection of Mercury in Urine.—Acidify about a liter of urine with 1 or 2 c.c. of hydrochloric acid, warm to 50°–60°, add half a gramme of zinc dust or freshly precipitated metallic copper (74). Stir vigorously half a minute and then filter. Metallic mercury is precipitated (88). Wash and confirm by heating in a tube (88).

Detection of Copper in Coloring Matter.—Digest the fabric

some time with concentrated ammonium hydroxid. A blue solution indicates copper (71).

Detection of Copper in Foods.—A large amount will be precipitated from the mass, after acidifying with hydrochloric acid, by means of iron, like a bright knife-blade (74). When washed and digested with concentrated ammonium hydroxid it makes a blue solution. If the amount of copper is small, it may be necessary to first destroy the organic matter by potassium chlorate (page 218).

Detection of Lead in Water.—Concentrate a large volume of water (one or more liters) to 100 c.c. in a dish with lead-free glazing, after adding one drop of nitric for each liter. If it is discolored by organic matter, remove this by potassium chlorate and hydrochloric acid (page 218). Then saturate with hydrogen sulphid gas, heat to boiling, filter and, after dissolving in nitric acid, confirm by lead tests (147, etc.).

Detection of Dangerous Amounts of Lead in Glazing or Enamel.—In the vessel to be tested boil for half an hour 4 per cent. acetic acid, adding water as it evaporates. Test the liquid after this time with hydrogen sulphid as above.

CHAPTER III

ANALYSIS BY MEANS OF THE BLOWPIPE

MANY of the important physical and chemical properties of the metals and their alloys which have not been shown by the preceding work can be demonstrated by the use of the blowpipe (page 15). These are often of the greatest importance in the technical use of the metals or the manufacture of their alloys, and they can best be learned by careful observation and long practice. They are such as are modified or are imparted to the metals by heating. By the same means some of the non-metallic elements and compounds undergo characteristic changes also.

Many metals, as well as some non-metallic substances, give characteristic reactions during or after heating alone or with some chemical agent. To obtain these first excavate a shallow cavity near one end of a stick of charcoal; place in this some of the substance equal to half a pea in size, and apply the blowpipe flame, using first the oxidizing flame, then the reducing (pages 15-16), and heating the charcoal underneath the assay as much as possible. The flame should be directed toward the unoccupied end of the charcoal so as to allow for a possible deposition of a coating.

In some cases the results are better observed if, instead of the charcoal, the assay is heated on a thin slab of plaster of Paris, made by pouring a thick mixture of this with water into a pasteboard box and letting it harden. For light-colored coatings it can, previous to using, be blackened by smoking.

I. The Non-metallic Substances and Metals of the Alkalies and Alkaline Earths

Water, if present in large amounts in the form of water of crystallization, as in alum, causes the substance to melt easily. When it has been evaporated by continued heating the anhydrous substance remains on the charcoal. If only a small quantity of moisture is present it will be necessary to heat the powdered solid in a glass tube when the moisture appears on the cool walls of the tube. Most hydroxids give up their water in this way.

Many *nitrates* and *chlorates* deflagrate when heated on charcoal, that is, appear to burn rapidly, leaving little visible residue. This is especially true of salts of the alkalies. Nitrates, when mixed with acid potassium sulphate and heated in a small glass tube, evolve a yellowish gas, best seen by looking down into the tube. This gas turns brown a slip of filter-paper which has been dipped in a solution of ferrous sulphate.

Chlorates yield oxygen, sometimes mixed with chlorine, when heated in a tube. If cupric oxid is dissolved in a bead of microcosmic salt by the aid of the oxidizing flame, when a chlorate is added the flame becomes azure-blue. Other *chlorine compounds* give the above reaction with the microcosmic bead and cupric oxid as do bromine compounds also. Many of them decrepitate, that is, fly to pieces when heated because of the moisture that is contained in the crystals, though this is not characteristic of chlorides.

Free sulphur and sulphids oxidize on charcoal in the oxidizing flame with the evolution of sulphurous oxid, recognizable by its odor.

Sulphates and other sulphur compounds, if they are fused on charcoal with dry sodium carbonate, and if then the fused mass is placed on a silver coin and moistened, will turn the

coin brown to black from the presence of sodium sulphid in the fused residue.

Silicates when heated on charcoal give no characteristic results. If fused in the bead of microcosmic salt their bases dissolve and the silica floats in a skeleton-like mass in the hot bead.

Organic compounds usually blacken when heated, although they do not always do so. If they contain no metals they are completely combustible or volatile.

Carbon can be burned completely. Graphite is combustible with difficulty before the blowpipe. It deflagrates when heated with potassium chlorate on platinum foil.

Sodium and potassium compounds melt and sink into the charcoal. Sodium gives a yellow flame; potassium, a violet one (pages 24-25).

Ammonium compounds volatilize completely, frequently leaving a distinct white coating on the charcoal.

The compounds of the *alkaline earths*, barium, strontium, calcium, and magnesium, remain white on ignition and often become highly luminous. They are sometimes infusible and sometimes melt and sink into the charcoal. Compounds of these metals that reduce to the oxids will turn moist litmus-paper blue when placed upon it.

Barium when held in the blue flame colors it yellowish-green. This may be made more perceptible by moistening the substance with a drop of hydrochloric acid. In the same way

Strontium gives a crimson-red, and

Calcium gives a yellowish-red flame.

Magnesium, when ignited, then moistened with cobalt nitrate solution and again ignited, is colored a faint flesh-pink.

Tests useful with Alloys and Amalgams

The student is to try the following tests and arrange the properties of each metal thus ascertained in a tabular form.

1. Mix as much of the oxid or carbonate of the metal as is equal to half the bulk of a pea with twice its volume of dry sodium carbonate and powdered borax. Heat in the reducing flame on charcoal as directed above. What is the action of these reagents at high temperatures? Note whether the compounds are reducible under these conditions and the ease with which this change can be effected. If the metal is obtained note its color and malleability.

Test in this manner, Hg, As, Sb, Sn, Bi, Pb, Cd, Mn, Cr, Fe, Co, Ni, Cu, Zn, Al, Ag, Au.

2. Heat on the charcoal stick, or on a plaster slab, a small fragment of the metal, not larger than one-tenth the size of a pea. Note and tabulate:

- (a) Degree of fusibility.
- (b) Ease of oxidation.
- (c) Color of coating, hot and cold.
- (d) Volatility of metal or of oxid as shown by position.

Test the same metals as under 1.

3. Place a small amount of the oxid or carbonate on a plaster slab, moisten with a drop of hydriodic acid, then heat with the oxidizing flame. Hold the colored films over ammonia; touch them with a drop of ammonium sulphid.

In this manner test Hg, As, Sb, Sn, Bi, Pb, Ag. On a sooted slab try similarly Cu, Cd, Zn.

4. After heating the oxid on charcoal or plaster moisten with a drop of cobalt nitrate solution, then heat thoroughly; test thus Sb, Zn, Sn, Al.

5. Dissolve a minute particle of the oxid in a borax bead by heating. Tabulate the colors of the beads, both hot and cold, after heating in the oxidizing, then in the reducing flame.

Test so Mn, Cr, Fe, Co, Ni, Cu.

6. Moisten a particle of the oxid or carbonate with hydrochloric acid and heat in the blue Bunsen flame on a platinum wire or an asbestos fiber. Why is the platinum wire less suitable as a support?

Test so Cu, Pb, Sb.

7. Heat in a small tube closed at one end, Hg, As, As_2O_3 .

II. The Common Heavy Metals Including the Alloys and Amalgams

1. Easily Volatile; Form a Coating or Disappear

Mercury is completely volatilized, leaving at most a distant, gray coating. On plaster this is very distinct. Some salts of mercury form white coatings. If mixed with dry sodium carbonate and heated in a tube, globules of mercury are deposited in the cool part of the tube. On plaster with sulphur and potassium iodid, or HI, it gives a scarlet coating with yellow; if quickly heated this is dull and black.

Arsenic volatilizes completely with distant white incrustation. It gives, when vaporized, a garlic odor. In a glass tube with sodium carbonate, most compounds give a dark ring with a metallic luster. This is metallic arsenic. No globules can be perceived.

Antimony gives brittle, white metallic globules. These produce white fumes when heated in the oxidizing flame and a distinct white incrustation with a bluish border. The metal continues to burn after removing from the flame, finally surrounding itself with crystals of the oxid. If dropped on the floor when melted it rolls and leaves a white track behind. It imparts a greenish-blue color to the oxidizing flame. Heated on plaster with sulphur and potassium iodid, or HI, it gives an orange coating stippled with peach-red.

Bismuth gives reddish-white, brittle metallic globules with a yellow coating. When mixed with sulphur and potassium iodid, or HI, and heated with a small, oxidizing flame a brilliant scarlet coating is produced, with a yellow one at a greater distance; with the last reagents on plaster, a chocolate-brown coating appears with underlying scarlet; with ammonia this becomes orange-yellow and cherry-red.

Lead forms white, malleable metallic globules with a yellow coating which has a white edge. The flame is a bluish-white. Heated with sulphur and potassium iodid, or HI, the volatile coating is a bright yellow.

Cadmium has a reddish-brown incrustation near the assay with a yellow one farther away. No globules can be observed. If heated strongly in a glass tube the metal volatilizes, condensing to bright globules on cooling.

2. The Non-volatile Metals or those which Vaporize with Difficulty, and which Color the Borax Bead

Many of these impart a definite color to a bead of fused borax, held in a loop of platinum wire. To as far as possible avoid the presence of fusible metals which would alloy the platinum the test substance may be roasted on charcoal to vaporize the volatile ones and to oxidize most of the others, with any sulphur that may be present. This is accomplished by heating a thin layer with a gentle oxidizing flame so as not to fuse it, turning the particles in order to thoroughly oxidize or volatilize them. Some of the metals which may remain cannot be oxidized at all, and in many cases the oxidation is incomplete.

At the end of a platinum wire make a loop about an eighth of an inch in diameter by winding it around a match or the point of a pencil. Heat it, and after dipping it into powdered borax, heat the mass until it fuses to a clear, colorless bead. If this is colored, the wire was not clean and the bead should be removed by straightening the wire and a new one made. Touch the hot bead to a minute fragment of the oxidized residue which will adhere, then heat again, first in the oxidizing flame, then in the reducing flame of the blowpipe. Notice the color which is given to the bead. The latter should, with most metals, remain transparent. If it becomes black it is because too much of the substance has been added.

Manganese in the oxidizing flame gives a reddish-purple

which becomes colorless in the reducing flame. A small portion fused into a bead of potassium nitrate and sodium carbonate becomes deep green; a large amount gives a black color.

Chromium gives an emerald-green bead, there being little change produced by the different flames. In the bead of potassium nitrate and sodium carbonate, a yellow color is produced. If this mass is dissolved in a drop of water it makes a bright yellow solution.

Cobalt produces a deep blue bead, the color being unchanged in the reducing flame. Heated alone on charcoal in the reducing flame the metal is obtained—a black magnetic powder.

Iron colors the bead yellow to reddish in the oxidizing flame, the shade being darker when hot, and also as the amount of iron is increased. In the reducing flame it is colorless to bottle-green. Heated alone on charcoal, iron and its compounds give a black powder which is attracted by a magnet.

Nickel when oxidized gives a bead, violet when hot and brown when cold. With the reducing flame it is grayish or colorless. On the charcoal the reducing flame converts its compounds to metallic nickel, a black, magnetic powder. This shows a metallic luster on rubbing in a mortar.

Copper colors the borax green as it is taken from the oxidizing flame, changing to a blue as it cools. In the reducing flame the bead is colorless unless a large amount of the metal is present, when it becomes a brownish-red and opaque on cooling. On charcoal compounds of copper are reduced to the metal which fuses to a malleable globule. In the reducing flame the color of the metal is seen, but on removing it from the flame, or on heating in the oxidizing flame, it is covered with a black oxid. Copper gives a green color to the flame; the chlorid, which may be formed by moistening with hydrochloric acid, gives a blue one.

3. Metals which Volatilize with Difficulty or not at all and do not Color the Borax Bead

After heating, in order to as far as possible remove the volatile metals, if such are present, place the residue on a clean piece of charcoal and heat again with the oxidizing and then the reducing flame.

Zinc gives, near the substance, a coating which is yellow when hot and white after it has cooled. Moisten this with cobalt nitrate solution and heat again to as high a temperature as can be produced. The coating is changed to a bright green.

Tin has a coating, on or near the assay but no metallic globules. It is yellow when hot and white when cold. Moistened with cobalt nitrate solution and ignited, it becomes bluish-green. On plaster with sulphur and potassium iodid it gives a brownish-orange coating.

Aluminum gives a non-volatile incrustation on the substance heated, which is white both hot and cold. Ignition after moistening with cobalt nitrate solution produces a bright blue color.

Silver gives white, malleable metallic globules. A dark red coating is formed near the assay but only after very long heating.

Gold fuses to yellow metallic globules without a coating. It is soluble in aqua regia but not in nitric acid.

Platinum remains infusible on the charcoal and gives no coating. If reduced from its compounds it is a fine, black powder. If it is in larger masses it is of a white color.

Practical Exercises

By blowpipe analysis determine the metals in unknown compounds furnished by the instructors, then the names of unknown single metals, finally the composition of simple alloys.

To fix in mind the more important properties of the metals the following questions should in all cases be answered.

Ease of reduction? degree of fusibility? of volatility? ease of oxidation? difference at high temperatures and the ordinary ones? If an oxid is formed what is its color? is this changed with the temperature? is the metal malleable or brittle? hard or soft?

Try to classify the metals on the basis of each of these properties into

1. Very readily changed.
2. Changed without much difficulty.
3. Changed with difficulty.
4. No change effected.

Questions for Further Study on Blowpipe Analysis

For what reason is the charcoal under the test substances heated to a red heat in blowpipe analysis? What chemical action takes place when chlorates and nitrates are heated on charcoal? To what class of agents do these compounds belong? Where are they used when this property is of value? Are there any substances with which they would be incompatible? When is a high heat necessary to produce this chemical reaction? What is an acid salt? What is the action of the acid potassium sulphate when heated with a nitrate? Why does cupric oxid in the presence of a chlorate give a blue flame instead of the ordinary green one? How does moisture cause decrepitation? Why is it necessary to heat sulphur in order to obtain an odor? What is the black compound formed on a silver coin when it is brought into contact with moist sodium sulphid? Why must water be added before the discoloration can be produced? What brings about the change of a sulphate to a sulphid when treated in this manner? What becomes of the bases of a silicate when it is heated with microcosmic salt?

What is the black substance produced when organic compounds are heated? What compounds are formed when graphite is deflagrated with potassium chlorate? When ammonium chlorid is volatilized on charcoal is it a complete chemical decomposition or a physical change? Is calcium oxid fusible? What application is made of this property and the fact that it is very luminous at high temperatures? Why does the addition of hydrochloric acid to some of these compounds make a brighter flame? How do the compounds of the alkaline earths compare with those of the alkali metals in alkalinity? Are there any other of their compounds except the oxids which will have the same effect on litmus-paper?

What is the action of sodium carbonate in setting mercury free from its salts? Which would be the better way to detect small quantities of mercury by heating on charcoal or in a small tube? Is the sodium carbonate used for the same purpose with arsenic compounds? How would you explain the absence of metallic globules when cadmium, zinc, tin and aluminum compounds are heated on charcoal and their production when the same process is applied to compounds of lead or bismuth? Why is platinum wire used for supporting the borax bead in preference to wire of other metals? What causes the swelling of the powdered borax in making the transparent bead? How does the action of the borax in the bead explain its usefulness in the soldering of two pieces of metal? How can you explain the fact that some metals, like iron, give one color when the bead is heated in the oxidizing flame, and a different one in the reducing flame? What does the position of the coating on the charcoal show as regards the volatility of the metals?

THE REAGENTS MOST COMMONLY USED IN ANALYTICAL CHEMISTRY

When not otherwise stated the strength given is the weight of the reagent contained in a hundred parts of the solution and distilled water is the solvent.

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Acetic acid.	$\text{CH}_3\text{CO}_2\text{H}$	6		BaCl_2 (164); $\text{AgNO}_3 + \text{HNO}_3$ (225); no residue upon evaporation of 10 c.c.
Ammonium carbonate.	$(\text{NH}_4)_2\text{CO}_3$	10		BaCl_2 after acidifying with HCl (164); AgNO_3 after acidifying with HNO_3 (225); no residue upon igniting.
Ammonium chlorid.	NH_4Cl	10		BaCl_2 after acidifying with HCl (164); no residue upon ignition; no dark residue when evaporated to dryness.
Ammonium hydroxid.	NH_4OH	5	Dilute the stronger ammonia ¹ with water.	BaCl_2 after acidifying with HCl (164); equal volume of water and $\text{Ca}(\text{OH})_2$ (171); $(\text{NH}_4)_2\text{S}$ (Table II); no residue after evaporation; AgNO_3 after acidifying with HNO_3 (225).
Ammonium molybdate.	$(\text{NH}_4)_2\text{MoO}_4, 4\text{H}_2\text{O}$	5	Dissolve the salt in four parts of dilute ammonium hydrate, then slowly pour into 15 parts of 30% HNO_3 .	No yellow precipitate after several days' standing.

¹ "Stronger ammonia" is about 28%, not 100%.

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Ammonium oxalate.	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	5 As desired.	<p>Pass H_2S gas into three parts of ammonium hydroxid as long as it is absorbed. Then add two parts of ammonium hydroxid.</p> <p>Add flowers of sulphur to the last, and let it dissolve.</p> <p>3 parts of HCl, 1 part of HNO_3; should be freshly prepared.</p> <p>Is insoluble in water. To be shaken with water and used before settling.</p>	Same as carbonate.
Ammonium sulphid.	$(\text{NH}_4)_2\text{S}$			No residue on evaporation; no precipitation with MgSO_4 (10).
Yellow ammonium sulphid.	$(\text{NH}_4)_2\text{S}_x$			No colored residue on evaporation.
Aqua regia.				No insoluble residue with dilute HCl ; with this solution no precipitate by H_2S (Table IV) or NH_4OH and $(\text{NH}_4)_2\text{S}$ (Table II); dissolved in acetic acid no decolorization of a drop of indigo after warming with H_2SO_4 (239); $\text{HNO}_3 + \text{AgNO}_3$ (225).
Barium carbonate.	BaCO_3	5	<p>As BaCO_3, except last test.</p>	As BaCO_3 , except last test.
Barium chlorid.	$\text{BaCl}_2, 2\text{H}_2\text{O}$			No residue on evaporation over steam-bath.
Bromin water.	Br		<p>Add enough to water so that after shaking a few drops of Br remain in bottom.</p>	

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Calcium hydroxid.	$\text{Ca}(\text{OH})_2$		Saturate water with the pure hydroxid, and, after settling, decant or filter off the clear liquid. Must be kept away from air.	Should not remain clear when breathed into (171).
Cochineal.			In 100 parts of 20% alcohol macerate 1 part of powdered cochineal and, after settling, decant the clear liquid for use. Dissolve in water.	
Congo-red. Copper sulphate. Erdmann's reagent.	$\text{CuSO}_4, 5\text{H}_2\text{O}$	1 5	Add six drops of 40% nitric acid to 100 c.c. of water and to 10 drops of this solution add 20 gm. concentrated sulphuric acid. Dissolve 0.1 gm. of sodium molybdate in 10 c.c. of concentrated sulphuric acid. It must be freshly prepared as it is unstable.	
Fröhde's reagent.				
Ferric chlorid.	FeCl_3	5		$\text{K}_3\text{Fe}(\text{CN})_6$ (56); no strong odor of HCl from the solid; no color in the filtrate after precipitation by NH_4OH and no residue when this is evaporated. No red color with KSCN (57), no insoluble residue; but little change upon blue litmus paper; HCl and H_2S . (Table IV.)
Ferrous sulphate.	$\text{FeSO}_4, 7\text{H}_2\text{O}$	5	Dissolve in recently boiled water and preserve away from the air.	

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Hydrochloric acid (concentrated), sp. gr. 1.20.	HCl	40	One volume of the strong acid diluted with 8.5 volumes of water.	10 parts water and a few drops of BaCl ₂ (164); only very slight residue after evaporation; equal volumes of water and H ₂ S after an hour (Table IV); no color in solution.
Hydrochloric acid, dilute.	HCl	5	Place 10 grams of iodine in 50 c.c. of water and pass in H ₂ S gas until the color is light yellow, keeping it cold by setting vessel in ice water if necessary.	As with the concentrated acid.
Hydriodic acid.	HI		Generate the gas by the action of HCl or H ₂ SO ₄ on ferrous sulphid. To make the solution pass the gas into water as long as it dissolves. Keep away from air.	
Hydrogen sulphid.	H ₂ S		Dissolve enough indigo carmine to give the color desired. Dissolve in dilute alcohol. Should be kept in the dark.	
Indigo.	C ₂₀ H ₁₀ N ₂ O ₂	0.2		
Lacmoid.		5		
Lead acetate.	Pb(C ₂ H ₃ O ₂) ₂ , 3H ₂ O			With ammonium hydroxid no yellow color (54) or blue filtrate (71); HNO ₃ +AgNO ₃ (225); does not decolorize indigo when warmed with H ₂ SO ₄ (234).

Name.	Formula.	Percentage. Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Litmus solution.			Extract the powder with hot alcohol; discard this and extract with water, allow to settle and decant. Neutralize (purple color) with NaOH and H ₂ SO ₄ . Air must be allowed to enter the bottle in which it is preserved.	
Litmus paper.			Color the above solution red or blue by a drop of H ₂ SO ₄ or NaOH and saturate absorbent paper.	
Magnesium sulphate.	MgSO ₄ , 7H ₂ O	5		NH ₄ Cl + NH ₄ OH (188); H ₂ S (Table IV); HNO ₃ + AgNO ₃ (225).
Mercuric chloride.	HgCl ₂	5		No residue on ignition; no insoluble residue in water.
Metaphenylenediamin.	C ₆ H ₄ (NH ₂) ₂	0.5	Dissolve in water and acidify slightly with H ₂ SO ₄ .	There should be no color to the solution.
Methyl orange.	C ₁₄ H ₁₃ N ₃ O ₃ S	0.1		No precipitate with alkalis, or BaCl ₂ or brownish-yellow with HCl from con. solution; no violet or green with AuCl ₃ .
Methyl violet. Nessler's reagent.		1	Dissolve in water. 13 gm. HgCl ₂ in 800 c.c. of water, then 35 gm. KI when the precipitate should be dissolved. Add HgCl ₂ until a permanent turbidity forms, then 160 gm. KOH. Dilute to a liter; let it settle and use clear liquid.	

Name.	Formula.	Percentage. Strength.	Method of Preparation.	Should give Negative Results. when Treated as Follows:
Nitric acid (concentrated), sp. gr. 1.42.	HNO ₃	65-70		No residue on evaporation; after considerable dilution with water no reaction with BaCl ₂ (164); water + AgNO ₃ (225); ammonium hydroxid till alkaline, then (NH ₄) ₂ S (Table IV); and (NH ₄) ₂ CO ₄ (14).
Nitric acid, dilute.	HNO ₃	10	Dilute one volume of the concentrated acid with eight of water.	Same as for the concentrated acid.
Platinic chlorid.	PtCl ₄	1		Leaves no insoluble residue in alcohol.
Phenolphthalein.	C ₂₀ H ₁₄ O ₄	1	Dissolve in 50% alcohol.	No residue when dissolved in alcohol.
Potassium chromate.	K ₂ CrO ₄	1		HCl + BaCl ₂ (164); the solid warmed with equal parts of water and concentrated H ₂ SO ₄ gives no red fumes (Cl).
Potassium dichromate or bichromate.	K ₂ Cr ₂ O ₇	5		As the chromate.
Potassium cyanid.	KCN	5		No dark color in solid or in the precipitate with lead acetate (143); no insoluble residue in hot dilute alcohol.
Potassium ferricyanid.	K ₃ Fe(CN) ₆	5		No blue with FeCl ₃ (55).
Potassium ferrocyanid.	K ₄ Fe(CN) ₆ , 3H ₂ O	5		HCl + BaCl ₂ (164).
Potassium iodid.	KI	5		No blue color with limus; H ₂ S (Table IV); BaCl ₂ (164); FeCl ₃ + FeSO ₄ + NaOH + HCl (233); no blue color with starch solution and dilute H ₂ SO ₄ .

Name.	Formula.	Percentage. Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Potassium hydroxid.	KOH	5		5 gm. gives clear solution with 20 c.c. water; this when acidified with HCl and made alkaline with NH_4OH forms no precipitate on long standing (33); the filtrate or solution from the last gives no precipitate with $(\text{NH}_4)_2\text{S}$ (Table II) or $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (15); no residue in 90% alcohol; no results from $\text{HCl} + \text{BaCl}_2$ (164); $\text{HNO}_3 + \text{AgNO}_3$ (225); $\text{H}_2\text{SO}_4 + \text{indigo} + \text{heat}$ (239).
Potassium permanganate.	KMnO_4	0.1		0.5 gm. boiled with 2 c.c. alcohol and 25 c.c. of water, then HNO_3 added precipitates with neither $\text{Ba}(\text{NO}_3)_2$ (164) nor AgNO_3 (225); when decolorized by oxalic acid con. $\text{H}_2\text{SO}_4 + \text{FeSO}_4$ give no color (237). $(\text{NH}_4)_2\text{S}$ (Table II); BaCl_2 (164).
Potassium sulphocyanate. Rosolic acid. Silver nitrate.	KSCN AgNO_3	5 1 5	 Dissolve in 60% alcohol.	0.5 gm. with 0.5 c.c. water and 20 c.c. absolute alcohol leaves no insoluble residue (KNO_3 or AgCl).

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when treated as follows:
Sodium carbonate.	$\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$	10		After acidifying with HCl and evaporating to dryness no residue insoluble in water (SiO_2); with HCl + BaCl_2 (164); with HNO_3 + AgNO_3 (225); with $(\text{NH}_4)_2\text{S}$ or H_2S after acidifying.
Sodium hydroxid.	NaOH	5		Same as potassium hydroxid.
Sodium phosphate.	$\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$	5		With HCl no effervescence and with BaCl_2 no precipitate (164); HNO_3 + AgNO_3 (225); with strong H_2SO_4 does not decolorize indigo (239); H_2S (Table IV); $(\text{NH}_4)_2\text{S}$ (Table II).
Starch solution.	$(\text{C}_6\text{H}_{10}\text{O}_5)_x$	1	Mix with cold water, then heat to boiling. Decomposes on standing. See tests for nitrites.	
Sulphanilic acid.	$\text{C}_6\text{H}_4\text{NH}_2\text{SO}_3\text{H}$			
Sulphuric acid (concentrated), sp. gr. 1.84.	H_2SO_4	100		No dark color; no residue on evaporation; does not decolorize indigo (239); no precipitate on dilution with water or alcohol (147); no precipitate after neutralization with NH_4OH by $(\text{NH}_4)_2\text{S}$ (Table II) or $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (15); 10 volumes of water and AgNO_3 (225); Gutzeit's test (109).

Name.	Formula.	Percentage Strength.	Method of Preparation.	Should give Negative Results when Treated as Follows:
Sulphuric acid, dilute.	H_2SO_4	10	One volume is slowly poured into 17 volumes of water.	Same as with concentrated acid.
Tin chlorid for Bettendorf's test.	$SnCl_2$		One part of the crystallized salt in two parts of HCl, sp. gr. 1.19.	No color or precipitate on boiling;(111); water, and $BaCl_2$ (164).
Tin chlorid for Hg test.			Dissolve the metal in hot, concentrated HCl and dilute with water. Must have some undissolved metal in the liquid to be permanent.	Same as above.
Turmeric paper.			After washing the powdered turmeric root in water and drying, extract it with alcohol and with this solution saturate white paper.	
Vanadium sulphate.		0.5	Dissolve one part of ammonium vanadate in concentrated sulphuric acid.	

THE CHEMICAL ELEMENTS^{*}

with their Symbols and Atomic Weights

THESE are from the report of the International Committee on Atomic Weights, 1912.

NAME.	SYM- BOL.	AT. WT.	NAME.	SYM- BOL.	AT. WT.
Aluminum	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.2
Argon	A	39.88	Nickel	Ni	58.68
Arsenic	As	74.96	Niobium ²	Nb	93.5
Barium	Ba	137.37	Nitrogen	N	14.01
Beryllium ¹	Be	9.1	Osmium	Os	190.9
Bismuth	Bi	208.0	Oxygen	O	16.0
Boron	B	11.0	Palladium	Pd	106.7
Bromin	Br	79.92	Phosphorus	P	31.04
Cadmium	Cd	112.4	Platinum	Pt	195.2
Cæsium	Cs	132.81	Potassium	K	39.1
Calcium	Ca	40.07	Praseodymium	Pr	140.6
Carbon	C	12.0	Radium	Ra	226.4
Cerium	Ce	140.25	Rhodium	Rh	102.9
Chlorin	Cl	35.46	Rubidium	Rb	85.45
Chromium	Cr	52.0	Ruthenium	Ru	101.7
Cobalt	Co	58.97	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorin	F	19.0	Sodium	Na	23.0
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulphur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tu	168.5
Iodin	I	126.92	Tin	Sn	119.0
Iron	Fe	55.85	Titanium	Ti	48.1
Iridium	Ir	193.1	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.2
Lead	Pb	207.1	Xenon	X	130.2
Lithium	Li	6.94	Ytterbium	Yb	172.0
Lutecium	Lu	174.0	(Neo-ytterbium)		
Magnesium	Mg	24.32	Yttrium	Y	89.0
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.6	Zirconium	Zr	90.6
Molybdenum	Mo	96.0			

¹ Also called glucinum.

² Also called columbium.

The Metric System

IN all work in chemistry the metric system of weights and measures is used instead of the older ones formerly in vogue. It is based upon the meter (39.37 inches) which is the unit of length. The hundredth part of this is the centimeter and a cube of water at 4° C., each side of which is a centimeter, weighs a gramme—the unit of weight. One-tenth the length of the meter is a decimeter and a cube which has a side of this dimension contains a liter—the unit of capacity. The fractions and multiples of these are the following:

Measures of Length

10 millimeters (mm).	= 1 centimeter (cm.).
10 centimeters	= 1 decimeter.
10 decimeters	= 1 meter (m.).
10 meters	= 1 decameter.
10 decameters	= 1 hectometer.
10 hectometers	= 1 kilometer.

Measures of Weight

10 milligrammes (mg.)	= 1 centigramme.
10 centigrammes	= 1 decigramme.
10 decigrammes	= 1 gramme (g. or gm.).
10 grammes ¹	= 1 decagramme.
10 decagrammes	= 1 hectogramme.
10 hectogrammes	= 1 kilogramme (kilo.).

¹ The *me* is often dropped in the names of these denominations. It is perhaps preferable that it should be retained to avoid any danger of reading grain for gram.

Measures of Volume

10 milliliters = 1 centiliter.

10 centiliters = 1 deciliter.

10 deciliters = 1 liter (l.).

10 liters = 1 decaliter.

10 decaliters = 1 hectoliter.

10 hectoliters = 1 kiloliter.

In volumetric analysis it is important to remember that one cubic centimeter of water weighs one gramme, and that a liter contains 1,000 cubic centimeters. A liter of water therefore weighs 1,000 grammes or one kilogramme (kilo.).

For conversion into other systems we have:

1 meter = 39.37 inches.

1 foot = 0.304 meter.

1 liter = 61.03 cu. in. = 1.06 U. S. qts.

1 liter = 33.81 U. S. fluidounces.

1 gramme = 15.43 grains.

1 grain = 0.0648 gramme.

1 ounce (apoth.) = 31.1 grammes.

1 ounce (avoirdupois) = 28.35 grammes.

1 pound (apoth.) = 373.2 grammes.

1 pound (avoirdupois) = 453.6 grammes.

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1 - Ba, Sr, Mg, Na, K, Ca, #H₂.

2 - Co, Ni, Fe, Mn, Zn, Al, Cr.



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